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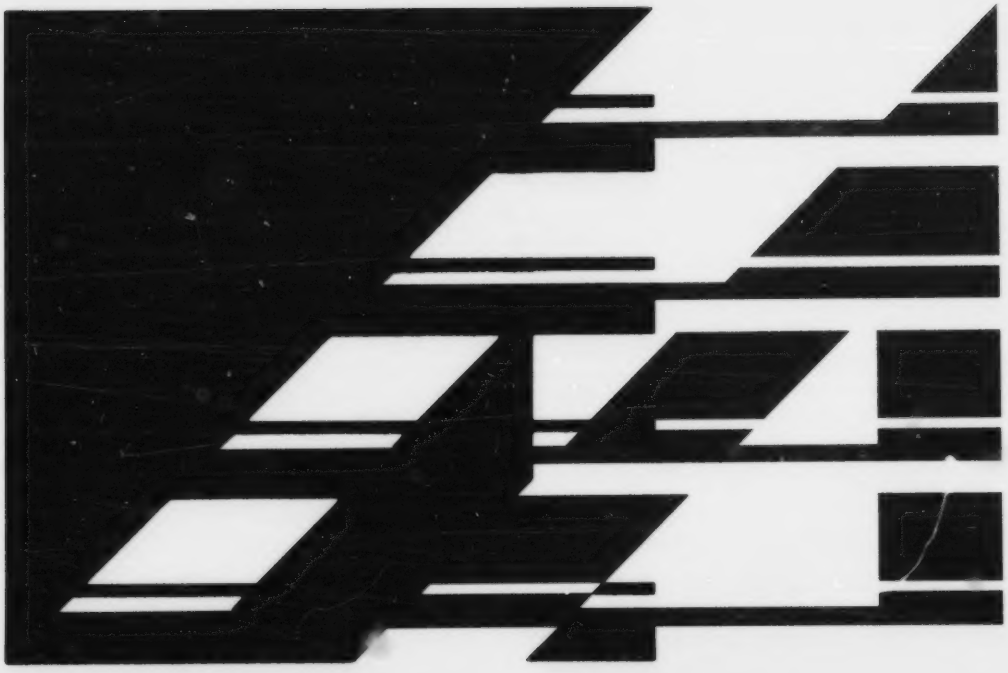

THE CHEMICAL ANALYSES OF NASICON POWDERS AND HYCERAM PELLETS

by

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ABSTRACT

Instrumental Neutron Activation Analysis (INAA) was used to determine the amount of sodium present in NASICON powders (x = 1.5) as a function of the extent of ion exchange in 0.2 molar HCl solutions. The INAA results showed not only that the conducting sodium was readily removed, but also that all the sodium (including structural) was removed. These results were quantitatively confirmed by ICP-AES analyses of the acid solutions used for the ion exchange.

X-ray diffraction (XRD) studies of the NASICON powders showed that there were slight changes in their XRD patterns; the fully exchanged Hydronium NASICON powder was found to be rhombohedral with slight but distinct changes in the hexagonal axis; the "a" axis was 2% smaller, but the "c" axis was 5% larger than for the precursor Na NASICON. The presence of an additional minor phase or phases in the fully exchanged samples was suggested.

1 Introduction

The chemical composition of the NASICON powders and the Hyceram pellets was studied in an effort to confirm whether the Hyceram pellets were in fact Bonded Hydronium NASICON. The initial concern was with the measurement of the amount of sodium remaining in the Hydronium NASICON. To achieve this, Instrumental Neutron Activation Analysis (INAA) was the primary analytical technique used. Other techniques, such as Induction Coupled Plasma Analysis (ICP), X-ray Fluorescence (XRF), and X-ray Diffraction (XRD) were also used to confirm the INAA findings and to obtain data on crystal structure and compositional information not obtainable by INAA.

2 Application of Instumental Neutron Activation Analysis to the Study of Hydronium NASICON and Hyceram

2.1 The Basis of INAA

Instrumental neutron activation analysis (INAA) starts by exposing the sample to be tested to a neutron flux for a specific period of time. During exposure, a minute fraction of the nuclei of the exposed sample absorbs an extra neutron. In most cases, this creates an unstable nucleus which undergoes β^- decay. If there is an associated gamma ray released during this decay, a gamma ray spectrometer can be used to detect the presence of the element which produced it.

The gamma rays emitted by the decaying nuclei have characteristic energies which enable the identification of the elements present in the sample according to the peaks appearing in the gamma ray spectrum. The area of a given peak can be used to determine the quantity of the element present in the material. Several factors must be taken into account in determining the relationship between the peak area and the amount of the element present in the sample.

These include:

(i) The thermal neutron capture cross-section and the magnitude of the resonance integral for each isotope.

(ii) The isotopic abundance of the unstable product's precursor.

(iii) The rate of decay of each of the products.

(iv) The emission of a gamma ray during the decay of the unstable nuclei.

(v) The absorption of gamma rays in the material under study.

(vi) The sensitivity of the detector as a function of gamma ray energy.

The use of standards in INAA is not difficult. The quantitative approach, requiring the evaluation of all of the previously stated factors, can be abandoned in favour of a simplified analysis performed on the basis of the results obtained from standards.

A readily available standard is the sodium precursor. It contains all of the sodium since it has not been sub-

jected to any exchange steps. The chemical formula (x = 1.5) of the sodium precursor is,

$$Na_{2.5}Zr_2P_{1.5}Si_{1.5}O_{12}. \quad (1)$$

A parameter, ε, may be introduced to represent the fraction of original sodium remaining in the material. Therefore the chemical formula for partially ion exchanged Hydronium NASICON is,

$$(Na_\varepsilon|(H_3O)_{1-\varepsilon})_{2.5}Zr_2P_{1.5}Si_{1.5}O_{12}. \quad (2)$$

When this material is exposed to a thermal and epithermal neutron flux in a nuclear reactor, several radiative capture reactions occur (Table 1).

Table 1 The expected nuclear reactions occurring in the Hyceram when it is exposed to a thermal and epithermal neutron flux [1,2,3].

	REACTION	DECAY CHARACTERISTICS OF THE PRODUCT: GAMMA RAY ENERGY [keV]	HALF LIFE
i	$^{23}Na + n \rightarrow ^{24}Na$	1369	15.02 h
ii	$^{96}Zr + n \rightarrow ^{97}Zr$	743.4	16.8 h
iii	$^{30}Si + n \rightarrow ^{31}Si$	1266	2.62 h
iv	$^{31}P + n \rightarrow ^{32}P$	no gamma	342.72 h
v	$^{29}Si + n \rightarrow ^{29}Al + p$	1273	6.5 m
vi	$^{28}Si + n \rightarrow ^{28}Al + p$	1779	2.24 m
vii	$^{31}P + n \rightarrow ^{28}Al + \alpha$	1779	2.24 m
viii	$^{27}Al + n \rightarrow ^{28}Al$	1779	2.24 m
ix	$^{27}Al + n \rightarrow ^{24}Na + \alpha$	1369	15.02 h

The absence of a gamma ray during the decay of ^{32}P excludes reaction iv from consideration. In addition, a preliminary neutron activation experiment with two samples of Hyceram (samples Hy288 and Hy471) demonstrated that no definable peak for the decay of ^{31}Si appeared in the spectrum. This was expected since there is a very low probability of gamma ray emission during the β^- decay of ^{32}P [2]. Therefore only two radiative capture reactions were of use (i & ii).

Reactions v, vi, vii, and ix can proceed when the target nucleus absorbs a fast neutron. Reaction viii involves thermal and epithermal neutrons and interferes with the analysis of ^{28}Si and ^{31}P (reactions vi and vii). Reaction ix produces ^{24}Na from ^{27}Al which causes a small error which can usually be ignored.

2.2 The Normalization of Peak Areas

It is common practice to normalize the peak areas with respect to the sample mass for the purpose of comparison with the standard. But Hydronium NASICON absorbs water which makes the sample mass dependent on the ambient relative humidity [4]. For Hyceram, phosphoric acid was added to the powder to effect bonding [4], which increases the mass of the sample and introduces error. For these reasons a second normalization factor was used as an alternative check on the results of the mass normalization method.

Table 2 The ICP data obtained for the Hydronium NASICON powder. Mass of each element found in the waste acid solutions in μg per 20 ml of solution. Each exchange step was performed on one gram of Hydronium NASICON and entailed one hour of treatment in HCl acid solution [10].

Element tested	No. of exchanges	Acid Concentrations [mol/litre] 0.2	0.5	1.0	2.0
Na	1	6441	7520	7259	10934
	2	2770	2420	2188	1981
	3	1476	1139	796	530
	4	878	575	408	115
	5	525	356	236	52
Total mass detected		12090	12010	10887	13612
Zr	1	<1	<1	<1	37
	2	<1	<1	5	128
	3	<1	<1	12	225
	4	<1	<1	27	182
	5	<1	1	32	179
Total mass detected		0	1	76	751
P	1	---	139	172	153
	2	---	47	56	20
	3	---	21	26	14
	4	---	9	16	11
	5	---	7	12	11
Total mass detected		---	223	282	209
Al	1	20	36	40	83
	2	20	18	30	35
	3	24	18	17	31
	4	24	11	21	19
	5	12	10	19	20
Total mass detected		100	93	127	188

By making reference to (2) (page 4) it is evident that the amount of zirconium in a sample of precursor is independent of x; furthermore, the ion exchange steps (Table 2, page 7) caused negligible reductions in the quantity of zirconium in the material, especially if performed in 0.2 M and 0.5 M HCl. Therefore the area of the zirconium peak is a good choice of normalization factor. In addition, the use of a ratio of two peak areas ensures that variations in the applied neutron flux, neutron flux depression within the material, sample moisture content, and the distance the irradiated sample is positioned from the counter, do not affect the result.

In a pure thermal neutron flux, one should not expect to obtain a significant peak for ^{97}Zr since both the neutron capture cross section (σ) of ^{96}Zr (0.022 barns) and its isotopic abundance (2.8%) are small (Table 3). But a typical thermal nuclear reactor also provides an epithermal flux which, by virtue of the ^{96}Zr's 5.1 barn resonance integral (I), is sufficient to produce a usable ^{97}Zr peak .

Table 3 The isotopic abundances and neutron capture cross-sections for the precursors of ^{97}Zr, ^{24}Na, and ^{28}Al [1].

	^{96}Zr	^{23}Na	^{27}Al
Isotopic Abundance	2.8%	100%	100%
Thermal neutron capture cross section (σ)	0.022 b	0.53 b	0.233 b
Resonance integral (I)	5.1 b	0.32 b	0.17 b

Although ^{30}Si and ^{31}P are not directly detectable, these isotopes react with the epithermal neutrons to produce ^{28}Al and ^{29}Al (Table 4).

Table 4 The nuclear reactions responsible for the creation of ^{28}Al and ^{29}Al [1, 3].

		DECAY CHARACTERISTICS OF THE PRODUCT	
	REACTION	**GAMMA RAY ENERGY [keV]**	**HALF LIFE**
i	$^{29}Si + n \rightarrow {}^{29}Al + p$	1273	6.5 m
ii	$^{28}Si + n \rightarrow {}^{28}Al + p$	1779	2.24 m
iii	$^{31}P + n \rightarrow {}^{28}Al + \alpha$	1779	2.24 m
iv	$^{27}Al + n \rightarrow {}^{28}Al$	1779	2.24 m

The products of the reactions shown in Table 4 can be detected provided the background is not too large and there is not an excessively long delay between removing the sample from the reactor and measuring the gamma ray spectrum. Unfortunately, the presence of trace amounts of ^{27}Al (reaction iv) in the material made it difficult to use the ^{28}Al peak as a means of measuring the amount of ^{31}P present; this is in addition to the difficulty caused by the contribution to ^{28}Al made by ^{28}Si (reaction ii).

To make better use of the ^{28}Al and ^{29}Al peaks, it is advantageous to wrap the sample in a cadmium foil before irradiating. Cadmium has a thermal neutron cross section of 2.45×10^3 barns as well as a 70 barn resonance integral [1, 5]. The cadmium can absorb most of the thermal neutron flux greatly reducing the activation of ^{27}Al, while having little effect on the production of ^{28}Al from ^{31}P, and ^{29}Al from ^{30}Si [5]. The use of these measurements as a means of estimating the amount of extra phosphorus in the bonded pellets was explored.

2.3 INAA Procedure

The samples were exposed to a neutron flux created by the SLOWPOKE nuclear reactor at the University of Toronto. The SLOWPOKE reactor can produce powers of 2, 5, 10, or 20 kW; for the studies of Hydronium NASICON and Hyceram, power levels of either 2 or 5 kW were used (2 kW corresponds to a neutron flux of 10^{11} $n.cm^{-2}.s^{-1}$), depending on the amount of sodium expected to be in the sample.

The irradiation time was selected to be 300 seconds. After irradiation, each sample was permitted to decay for nine minutes before its gamma ray spectrum was obtained on a Canberra 8180 germanium detector-based gamma ray spectrometer, using a five minute count period. The delay permitted the gamma radiation released by the decay of ^{97}Zr to achieve equilibrium (Fig. 1), and it allowed short-lived isotopes such as ^{28}Al and ^{29}Al to decay, which reduced the overall background level in the gamma ray spectrum (see Fig. 2, page 13 for two examples of typical gamma ray spectra). Sodium content was determined on the basis of the $^{23}Na(n,\gamma)^{24}Na$ (E_γ 1368 keV, $t_{\frac{1}{2}}$ 15 hours) nuclear reaction, and zirconium content was determined from the reaction $^{96}Zr(n,\gamma)^{97}Zr$ (E_γ 743 keV, $t_{\frac{1}{2}}$ 16.8 hours) [1, 2]. If during the testing of a sample there was some departure from these times, the appropriate decay correction calculations were made, where necessary.

All specimens (powder or pellet) were weighed and placed in small (1.2 ml) plastic vials. The use of sealed vials permitted the samples to be irradiated, without loss of material during the experiment or during subsequent storage.

Zirconium-97 (^{97}Zr) decays to either ^{97}Nb (ground state) or $^{97}Nb^*$ (excited state). The decay of ^{97}Zr to the latter proceeds without the emission of the 743.4 keV gamma ray. This gamma ray will be emitted when the $^{97}Nb^*$ decays

to its ground state, with a half life of 54 seconds (t_I) [1].

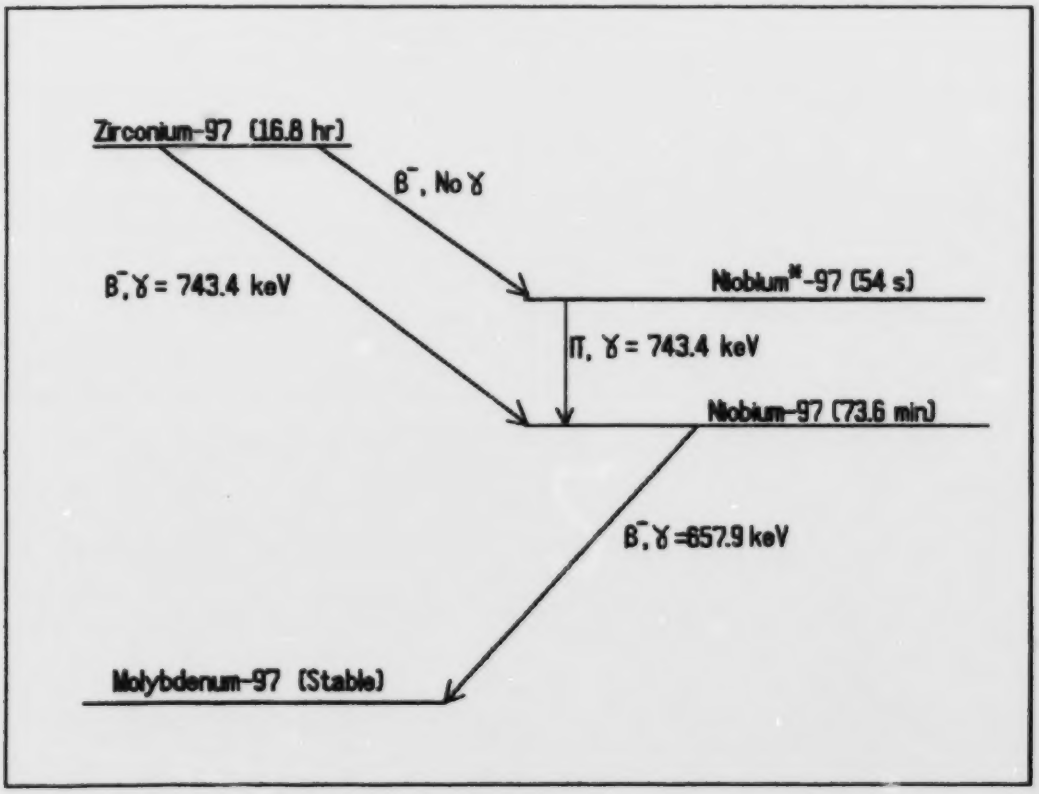
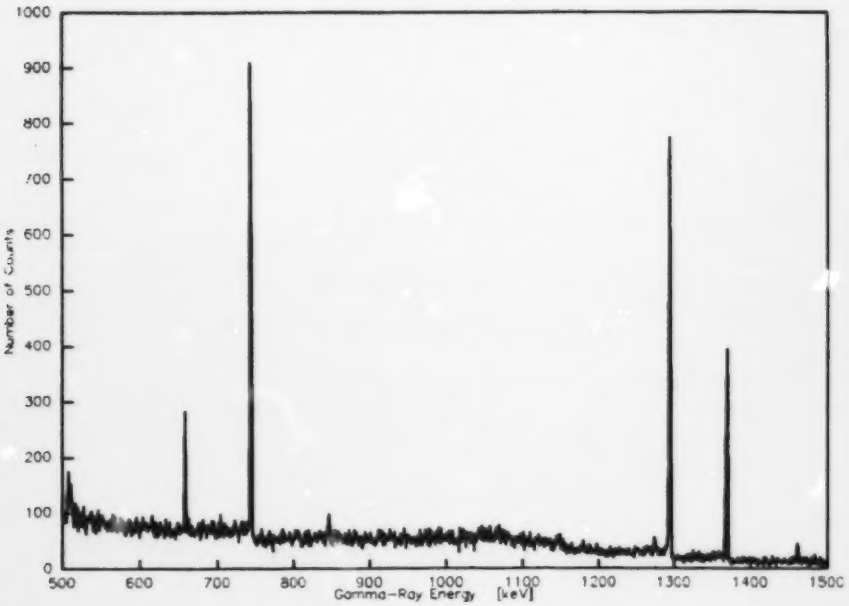
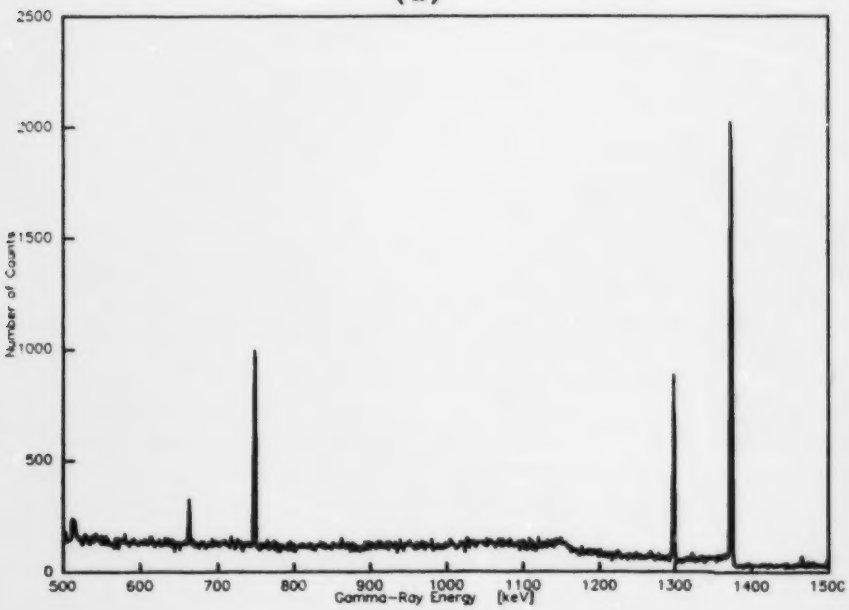


Fig. 1 The decay scheme of ^{97}Zr. The isotopes' half lives are indicated in brackets. The mode of decay (i.e. β^- decay, or Isotropic transformation "IT") is shown beside the transformation energy of the associated gamma ray. [1].



(a)



(b)

Fig. 2 Two examples of a gamma ray spectra for Hyceram pellets. Note the shape of the background. Sample Hy486b is shown in (a) and sample Hy231a is shown in (b).

Since the half life of ^{97}Zr ($t_{1/2}$) is 16.8 hr (i.e. 60,480 sec) one may consider $t_{1/2} >> t_I$. Therefore of those ^{97}Zr nuclei which decay to $^{97}Nb^*$, there will eventually be a corresponding and equal rate of gamma emission arising from the isomeric transformation of the $^{97}Nb^*$. For this equilibrium state to be attained, a waiting period of t seconds (where $t >> (t_{1/2} \times t_I)/(t_{1/2} - t_I)$) must transpire [5]. Since $(t_{1/2} \times t_I)/(t_{1/2} - t_I) \approx t_I = 54$ seconds, the nine minute period chosen corresponds to 10 x t1. Therefore one may assume that equilibrium will be achieved during the nine minute delay.

Circumstances were sometimes such that a period longer than the prescribed nine minutes transpired (perhaps as long as 15 minutes). In this case, a correction factor was calculated from the following ratio.

$$Q(t) = \frac{\mathrm{Exp}\left[\frac{-t \times \ln(2)}{15.02 \times 60}\right]}{\mathrm{Exp}\left[\frac{-t \times \ln(2)}{16.8 \times 60}\right]} \qquad (3)$$

where t represents the time (in minutes), which has elapsed since the sample was removed from the SLOWPOKE reactor. The number, 15.02, in Equation 3 is the half life of ^{24}Na (in hours) and, 16.8, is the half life of ^{97}Zr (in hours). Some values for typical times (t) are shown in Table 5. From

these tables, it was concluded that the error in the sodium activity to zirconium activity ratio arising from a delay exceeding nine minutes was negligible.

The errors in the actual ^{97}Zr and ^{24}Na activities which arise from the time delay were also calculated (Table 6). It was found that the amount of relative decay during the first 30 minutes was not considerable.

Table 5 The values of Q(t) (Equation 3) where the required correction factor is Q(t)/Q(9).

t [min]	Q(t)	Correction Factor
0	1.0000	---
9	0.9993	1.000000
10	0.9992	1.000082
11	0.9991	1.000163
12	0.9990	1.000245
13	0.9989	1.000326
14	0.9989	1.000408
15	0.9988	1.000897
20	0.9984	1.000489
30	0.9976	1.001713
60	0.9951	1.004165

Table 6 The reduction in ^{97}Zr and ^{24}Na activities with respect to time, t. At t = 0, ^{97}Zr = ^{24}Na = 1.0000.

t [min]	^{97}Zr	^{24}Na
0	1.0000	1.0000
9	0.9938	0.9931
10	0.9931	0.9923
11	0.9925	0.9916
12	0.9918	0.9908
13	0.9911	0.9901
14	0.9904	0.9893
15	0.9897	0.9885
30	0.9796	0.9772
60	0.9596	0.9549

A gamma ray spectrum is composed of several peaks superimposed on a contiguous background. To obtain the net activity for a particular isotope required that the appropriate peak first be identified and then the gross peak area be reduced by the local background. By following this procedure a net peak area proportional to the activity of the isotope which produced the peak was obtained. It was advantageous to measure the left background (BL) and the right background (BR), since the background can be different on either side of a peak, depending on where it appears in the spectrum (Fig. 3).

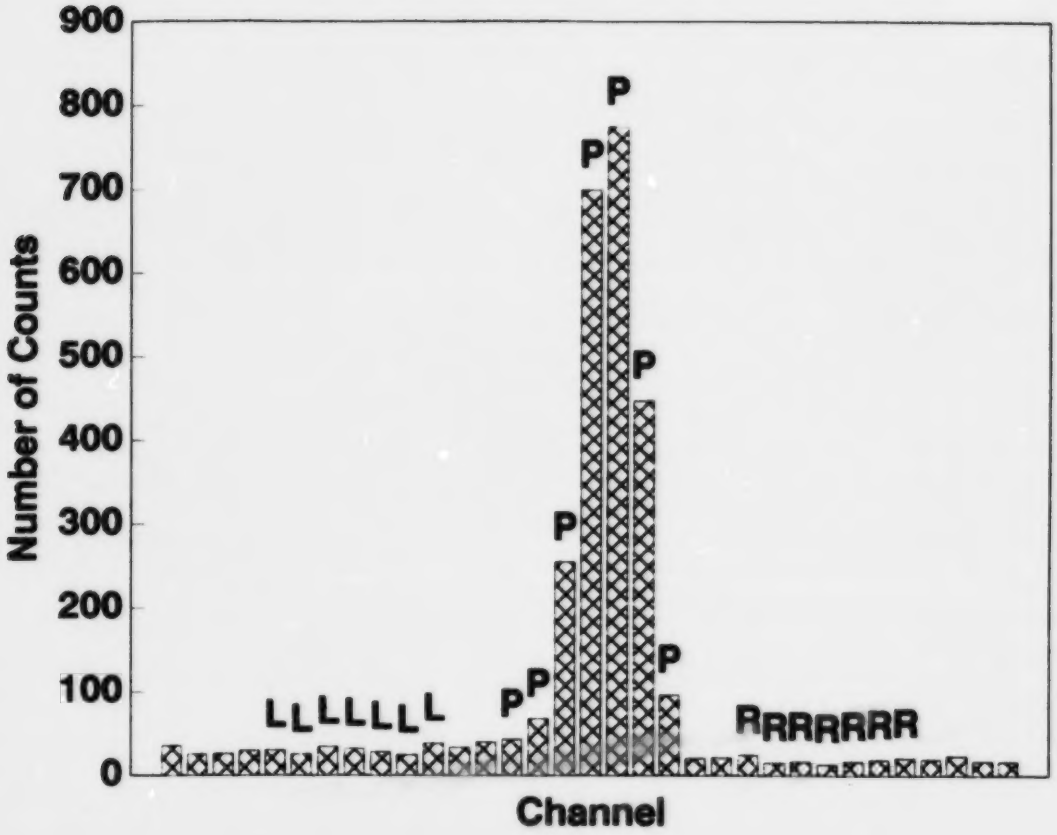


Fig. 3 A schematic representation of a gamma ray peak. The net peak is obtained by subtracting the average of the two background areas (BL & BR) from the gross peak (P).

2.4 The Statistics of Counting with Respect to Gamma Ray Peaks

It has been shown [6] that the error (one standard deviation) in peak area is equal to $(n_p)^{\frac{1}{2}}$, where n_p is the number of counts corresponding to the peak of interest. Therefore one may be 95% confident that the true number of counts is in the interval $n_p \pm 2(n_p)^{\frac{1}{2}}$. This is also true for the number of counts measured in the background where the 95% confidence interval is $n_b \pm 2(n_b)^{\frac{1}{2}}$.

In general, one may calculate the 95% confidence interval for a sum or difference, viz,

$$(X \pm x) + (Y \pm y) = (X + Y) \pm (x^2 + y^2)^{\frac{1}{2}}, \qquad (4)$$

or

$$(X \pm x) - (Y \pm y) = (X - Y) \pm (x^2 + y^2)^{\frac{1}{2}}. \qquad (5)$$

From Equation 5 the number of counts in the net peak would be (95% confidence),

$$n_{net} = (n_p - n_b) \pm 2(n_p + n_b)^{\frac{1}{2}}. \qquad (6)$$

From Equations 4 to 6, the experimental errors can be calculated from the gamma ray spectrum.

When calculating the 95% confidence interval for the ratio of ^{24}Na activity to ^{97}Zr activity the following relationship was used [7].

$$\frac{(X \pm x)}{(Y \pm y)} = \frac{X}{Y} \pm \frac{X}{Y}\left[\left[\frac{x}{X}\right]^2 + \left[\frac{y}{Y}\right]^2\right]^{1/2} \qquad (7)$$

When using percent errors Equation 7 simplifies to Equation 8.

$$\frac{(X \pm x\%)}{(Y \pm y\%)} = \frac{X}{Y} \pm \left[x\%^2 + y\%^2 \right]^{1/2} \qquad (8)$$

From this, the 95% confidence interval for the mean of N results can be derived in the form of Equation 9.

$$1/n \sum_i^n \{ X_i \pm x_i \} = X_{mean} \pm 1/n \left(\sum_i^n x_i{}^2 \right)^{1/2} \qquad (9)$$

where x_i represents the 95% confidence interval (absolute error) for the i^{th} measurement.

The foregoing equations are used for determining the values of standard error for the experimental results. Therefore, the 95% confidence interval for a set of experimental results for a particular specimen is calculated on the basis of Equation 9. The individual errors used in this

equation are determined by either EQUATIONS 7 or 8 which in turn are based on the results of Equation 6 (page 18).

2.5 Correction Factors for Distance from Detector

The gamma ray spectra were obtained by placing the irradiated sample at a prescribed distance from the gamma ray detector. Whenever possible the sample was placed in position Po- the closest location possible. But in circumstances where the sample was producing a large amount of radiation, the counter's deadtime# became too great (20%), which required the specimen to be positioned farther away from the detector. The distance was selected to make the deadtime about 15%. The peak areas were adjusted with respect to position Po by multiplying by the appropriate correction factor (Table 7).

Deadtime is the fraction of time during which the counter is processing an incoming pulse; during this time it is unable to respond to gamma ray energy.

Table 7 The correction factors required when adjusting peak areas obtained from a sample at position Px with respect to position Po. The larger the value of x, the further away the specimen was positioned from the counter.

Position number X	Correction factor Po/Px
0	1.00
1	1.29
3	1.69
4	2.21
5	3.50
6	5.07
7	7.06
8	9.17
9	14.5
10	20.8

A sample's residual sodium is proportional to its ^{24}Na to ^{97}Zr ratio. Therefore knowing the ratio for the Na NASICON precursor allows one to determine the fraction of original sodium remaining in the Hydronium NASICON or Hyceram pellet. A number of irradiations of Na NASICON powder were performed to obtain an average $^{24}Na/^{97}Zr$ ratio. This average ratio and the experimental error were used throughout the calculations of the sodium residue of the exchanged powders and Hyceram pellets.

2.6 The Hypothetical Ratio of ^{24}Na counts to ^{97}Zr counts

If the fractions of thermal neutrons and epithermal neutrons in the SLOWPOKE reactor's flux are known, one can calculate the theoretical ratio of ^{24}Na activity to ^{97}Zr activity, viz,

$$\frac{^{24}Na}{^{97}Zr} = \text{Material Factor} \times \text{Neutron Capture Factor} \times \text{Detector Efficiency Factor}$$

$$= \frac{M_{Na} \times A_{23Na} \times \tau_{97Zr}}{M_{Zr} \times A_{96Zr} \times \tau_{24Na}} \times \frac{\Phi_{Thermal} \times \sigma_{23Na} + \Phi_{Epi} \times I_{23Na}}{\Phi_{Thermal} \times \sigma_{96Zr} + \Phi_{Epi} \times I_{96Zr}} \times \frac{\eta_{24Na}}{\eta_{97Zr}} \quad (10)$$

Where $$\Phi_{Thermal} + \Phi_{Epi} = \Phi. \quad (11)$$

For the Material Factor: M_{Na} and M_{Zr} are the respective number of moles of sodium and zirconium in one mole of NASICON; A_{23Na} and A_{96Zr} are the respective isotopic abundances of ^{23}Na and ^{96}Zr; and τ_{97Zr} and τ_{24Na} are the respective half lives of ^{97}Zr and ^{24}Na.

For the Neutron Capture Factor: $\Phi_{Thermal}$ is the flux of thermalized neutrons in the SLOWPOKE reactor; Φ_{Epi} is the flux of neutrons which are still in the epithermal energy range; and Φ is the total flux. Sigma (σ) and, I, have the usual meaning: σ, represents thermal neutron capture cross-section and, I, represents the resonance integral (Table 3, page 8).

Finally, the Detector Efficiency Factor is the quotient of η_{24Na} and η_{97Zr}: the efficiencies of the detector at 1369 keV and 743.4 keV, respectively. Since the detector's efficiency drops considerably with increasing energy these factors must also be included.

The substitution of the accepted values into the Material Factor yields the following intermediate equation:

$$\frac{^{24}Na}{^{97}Zr} =$$

$$= \frac{2.5 \times 100\% \times 16.8h}{2.0 \times 2.8\% \times 15.02h} \times \frac{\Phi_{Thermal} \times \sigma_{23Na} + \Phi_{Epi} \times I_{23Na}}{\Phi_{Thermal} \times \sigma_{96Zr} + \Phi_{Epi} \times I_{96Zr}} \times \frac{\eta_{24Na}}{\eta_{97Zr}}$$

$$= 49.9 \times \frac{\Phi_{Thermal} \times \sigma_{23Na} + \Phi_{Epi} \times I_{23Na}}{\Phi_{Thermal} \times \sigma_{96Zr} + \Phi_{Epi} \times I_{96Zr}} \times \frac{\eta_{24Na}}{\eta_{97Zr}} \qquad (12)$$

It is possible to evaluate the Neutron Capture Factor if $\Phi_{Thermal}$ and Φ_{Epi} are known.

At this point, the theoretical $^{24}Na/^{97}Zr$ ratio can be estimated on the basis of the neutron flux for the type of reactor at the University of Toronto's SLOWPOKE facility. The value of Φ_{Epi}/Φ has been estimated to be 5% [8]; therefore $\Phi_{Thermal}/\Phi$ is 95%. From this, one finds that the Neutron Capture Factor is equal to 1.88.

The Detector Efficiency Factor for 743.4 keV and 1369 keV gamma rays is estimated to be 0.5. Therefore, the $^{24}Na/^{97}Zr$ ratio for the stoichiometric precursor is 49.9 x

1.88 x 0.5 = 46.9. This value was used to test the validity of the experimental results obtained for the precursors.

3 Analytical Techniques in Addition to INAA

In addition to being effective for measuring the concentrations of sodium and zirconium, it was found that INAA is also an effective means of determining the degree of ion exchange effected by the acid treatments, as well as estimating other characteristics of the powder. During the formative stages of the research, it was considered necessary to perform tests of the powders and waste acid solutions. ICP was performed on the waste acid solutions by the chemistry branch of the Chalk River Nuclear Laboratories (CRNL), XRF was performed in the Metallurgy and Materials Science Department at the University of Toronto, and XRD was performed at CANMET prior to shipping the NASICON powders to Toronto.

3.1 ICP

The waste acid solutions left after each ion exchange step were subjected to ICP analysis. This permitted a check on the INNA results as well as determining the loss of other components (i.e. Zr, Si, P) during the acid treatment. If excessive quantities of the elements other than sodium entered the acid solution, then the assumption of constant zirconium content would be in doubt.

3.2 XRF

The NASICON powders were analysed directly by XRF as a further test of each powder's composition. Since sodium has a low atomic number, it was not as accurately measured by XRF as it would be by INNA or ICP; but the other elements in NASICON were measured by XRF with acceptable accuracy.

A Philips PW1400 X-ray fluorescence analysis system, which had been used extensively for the analysis of slags (slags are generally composed of oxides), was available; this meant that a wide range of standards had already been analysed.

The analysis of a sample required that it first be ground to a powder. Since the material's crystal lattice would cause interference patterns during the X-ray analysis, it was necessary to combine the powder (one gram) with $Li_2B_4O_7$ to produce a glass disc. The glass disc was exposed to the X-ray beam for analysis.

3.3 XRD

Determining the powder's composition after each exchange step was necessary to test the validity of the INNA results, it was also necessary to record the X-ray diffraction pattern of the NASICON as ion exchange proceeded. It was then possible to observe if a change in the sample's basic crystal structure had occurred as a result of the removal of sodium. A change in crystal structure would inval-

idate the INNA results since a new product, other than a NASICON, would have been created by the ion exchange process.

Work has been performed previously on the crystal structure of NASICON [12, 13]. The indexing of the Na NASICON (x=2) at 500°C [13] served as the basis for indexing the Na NASICON precursor (x = 1.5) and the Hydronium NASICON product [14].

4 Sample Characteristics

4.1 Sample Preparation

Two physical types of sample were tested: NASICON powders, and Hyceram pellets.

The powder samples were prepared at CANMET specifically for the INNA study. Starting with a Na NASICON precursor (x = 1.5), three 12 hour exchange steps in 0.2 M HCl at 90 °C followed by a final exchange step in 0.5 M HCl at 90 °C were performed. After each step a small sample of powder was retained for analysis.

A second series of powders was subsequently prepared with exchange times based on short initial periods followed by longer exchange times. Each exchange step was performed in 0.2 M HCl at 90 °C. The purpose of testing a second series was to attempt to gain a more complete picture of the evolution of the sodium content of the NASICON with respect to exchange time. Samples of waste acid taken after each exchange were sent to the CRNL for analysis of sodium, zirconium, silicon, and phosphorus content by ICP. Before

INNA was performed, X-ray diffraction patterns for each sample where obtained at CANMET. After INNA, the powders were submitted for X-ray fluorescence analysis (XRF).

A third set of powder samples, composed of precursors with x = 0, x = 1.5, and x = 2.0, was prepared for additional ion exchange experiments. The INNA results for these three precursors helped to verify the sodium residues obtained for the other samples. X-ray diffraction patterns were also recorded for the third series of samples.

The Hyceram pellets consisted of four series. The first series (Hy100 series) represented the first batch of pellets manufactured at CANMET. The Hy200 and Hy300 series were manufactured later. All three of these series were made from Hydronium NASICON which had been exchanged once. The final series of pellets (the Hy400 series) was composed of Hydronium NASICON which had been exchanged four times.

4.2 Series One

Tables 8 and 9 present the sample characteristics for the first series of samples to be tested. Included in this series of tests are the Hyceram pellets.

The powders were in two forms, dried and calcined. The calcined powders had been irreversibly dehydrated as a result of the destruction of the crystal lattice; in a previous study [4], XRD patterns confirmed that calcined Hydronium NASICON powders are amorphous [4].

Table 8 The first series of NASICON powders tested by INAA.

Sample number	Mass [mg] a	b	c	Sample characteristics
1	131.3	120.5	17.3	Na NASICON precursor. Calcined at 800 C.
2	206.5	287.1	---	Na NASICON precursor. Calcined at 1250 C.
3	153.9	204.7	---	Subjected to a single exchange 12 hours in 0.2 M HCl. Dried for one hour at 90 C.
4	181.6	138.1	---	Same as 3 but also calcined at 900 C.
5	177.5	190.1	---	Subjected to a second exchange step - 12 hours in 0.2 M HCl. Dried for one hour at 90 C.
6	212.0	219.5	---	Same as 5 but also calcined at 900 C.
7	139.7	115.5	16.0	Subjected to a third exchange step - 12 hours in 0.2 M HCl. Dried for one hour at 90 C.
8	151.1	102.5	---	Same as 7 but also calcined at 900 C.
9	159.6	179.9	29.2	Subjected to a fourth exchange step - 12 hours in 0.5 M HCl. Dried for one hour at 90 C.
10	166.2	156.4	---	Same as 9 but also calcined at 900 C.

Table 9 The pellets of Hyceram analysed by INAA.

Sample number	Mass [mg] a	b	Brief Description
Hy146	88.2	63.8	One of the earliest Hyceram pellets to be produced.
Hy206	55.7	60.8	Covered with Platinum paste.
Hy231	53.1	73.0	No Pt paste.
Hy288	63.5	55.4	No Pt paste.
Hy319	73.9	45.3	Covered with Pt paste.
Hy328	41.5	51.3	No Pt paste.
Hy347	70.1	64.9	No Pt paste.
Hy392	49.4	55.1	No Pt paste.
Hy393	55.5	85.4	No Pt paste.
Hy396	56.0	49.0	No Pt paste.
Hy471	48.9	40.4	No Pt paste.
Hy477	72.2	70.9	No Pt paste
Hy486	61.6	44.5	No Pt paste.

The objective of performing INAA on the pellets was to determine the amount of residual sodium. This information was considered important in light of the effort to characterize the conductivity of Hyceram.

To manufacture a pellet from Hydronium NASICON powder required the addition of a quantity of phosphoric acid. The phosphoric acid was believed to react with zirconium in the NASICON powder to form zirconium phosphate, a protonic conductor in its own right [9, 4]. Since the procedure for mixing the phosphoric acid and Hydronium NASICON powder was not quantified, one could not be certain of the amount of additional water and phosphorus which was added to the specimen. It was the presence of this additional, unknown quantity of material which complicated the measurement of residual sodium (mass dilution effect). This was particularly true since the preparation of each sample would be performed slightly differently from the others. In addition, there was a quantity of platinum painted onto the faces of some pellets; this lead to further mass dilution. Fortunately, the use of the zirconium peak area in the gamma ray spectrum as a normalization factor permitted a check on the sodium residuals calculated on the basis of sample mass.

4.3 Series Two

An attempt was made to gain a more detailed picture of the relationship between sodium residue and ion exchange time. Table 10 lists the samples used.

Table 10 Second series of NASICON powder tested by INAA.

Sample number	Mass [mg] a	b	Brief Description
30	124.8	122.8	Na NASICON powder. Used as precursor for this exchange series.
31	119.4	214.3	Exchanged once, 30 minutes. 0.2 M HCl.
32	152.1	200.8	Exchanged twice, total 1 hour. 0.2 M HCl.
33	210.7	171.4	Exchanged three times, total 2 hours. 0.2 M HCl.
34	105.3	207.0	Exchanged four times, total 4 hours. 0.2 M HCl.
35	244.9	345.3	Exchanged five times, total 8 hours. 0.2 M HCl.
36	227.4	243.9	Exchanged six times, total 16 hours. 0.2 M HCl.
37	288.1	328.7	Exchanged seven times, total 32 hours. 0.2 M HCl.

4.4 Series Three

Although the Na NASICON precursors were carefully prepared, it was considered necessary to perform a sodium analysis by INAA on two other types of precursor: x = 0, and x = 2, as a final confirmation of the validity of the analysis method. Table 11 lists the samples used.

Table 11 The set of NASICON precursors.

Sample number	Sample Characteristics
1000	Na NASICON precursor, x = 0.
2000	Na NASICON precursor, x = 1.5.
3000	Na NASICON precursor, x = 2.0.

5 Experimental Results For the NASICON Powders

5.1 Series One

Table 12 summarizes the values obtained for the first series of powders. A calculation of experimental error is included.

Table 12 A tabulation of the specific activities of ^{24}Na, ^{97}Zr, and the $^{24}Na/^{97}Zr$ ratio for the first set of NASICON powders.

sample Number	^{24}Na/mg	^{97}Zr/mg	$^{24}Na/^{97}Zr$
S	6.6×10^{3}^	140+	46.9*
1	$6.3 \times 10^{3} \pm 20$	137 ± 8	45.0 ± 2.6
2	$6.5 \times 10^{3} \pm 20$	141 ± 10	45.8 ± 3.5
3	$1.03 \times 10^{3} \pm 10$	156 ± 3	6.5 ± 0.2
4	$1.06 \times 10^{3} \pm 10$	167 ± 4	6.2 ± 0.1
5	301 ± 4	157 ± 3	1.9 ± 0.1
6	334 ± 4	170 ± 3	1.9 ± 0.1
7	147 ± 2	174 ± 3	0.84 ± 0.02
8	164 ± 2	186 ± 3	0.87 ± 0.02
9	48.2 ± 1.1	171 ± 2	0.28 ± 0.01
10	49.3 ± 1.1	179 ± 2	0.27 ± 0.01

* A result for a stoichiometric sample of NASICON (x = 1.5) which is assumed to have been irradiated in the SLOWPOKE reactor.

\+ Based on measurement of ZrO_2 standard.

^ Based on ^{97}Zr/mg multiplied by $^{24}Na/^{97}Zr$.

Sample "S" represents a set of results for a stoichiometric sample of Na NASICON (x = 1.5) which is assumed to have been irradiated in the SLOWPOKE reactor. The values for "S" compare favourably with the experimentally obtained results.

Since the difference between the $^{24}Na/^{97}Zr$ ratios for the two types of precursor was not significant, the two values were incorporated into a single standard value of 45.3 ± 2.1, which was used for determining the sodium residues and confidence intervals in Table 13.

The sodium residues (ratio method) for the calcined (even numbers) samples did not differ greatly from the sodium residues of their dried counterparts, indicating a negligible loss of sodium during the heat treatment.

But the specific ^{24}Na activities for the calcined samples all had higher values than their dried counterparts; a result of the loss of water during the heat treatment. Water loss reduced the sample's mass, which increased the amount of ^{24}Na per unit sample mass.

The specific ^{24}Na counts for the exchanged powders can be divided by the specific ^{24}Na counts for the precursor to yield estimates of the residual sodium levels for each sample. Table 13 presents these values (mass normalization) including the sodium residues calculated by the ratio method.

Table 13 The sodium residues for the exchanged powders calculated on the basis of the mass normalization method. The results of the ratio method are shown in the second column.

Sample Number	Sodium res. mass method [%]	Sodium res. ratio method [%]
1 and 2	100 ± 0.4	100 ± 5
3	16.3 ± 0.12	14.4 ± 0.5
4	16.8 ± 0.14	13.6 ± 0.5
5	4.76 ± 0.06	4.14 ± 0.14
6	5.28 ± 0.06	4.25 ± 0.14
7	2.31 ± 0.04	1.85 ± 0.05
8	2.59 ± 0.04	1.93 ± 0.05
9	0.76 ± 0.02	0.62 ± 0.02
10	0.78 ± 0.02	0.59 ± 0.02

The sodium residue values calculated by the ratio method are plotted in Fig. 4. The form of the plot is much the same as that in Fig. 6 which also shows the sodium residues calculated by the mass normalization method.

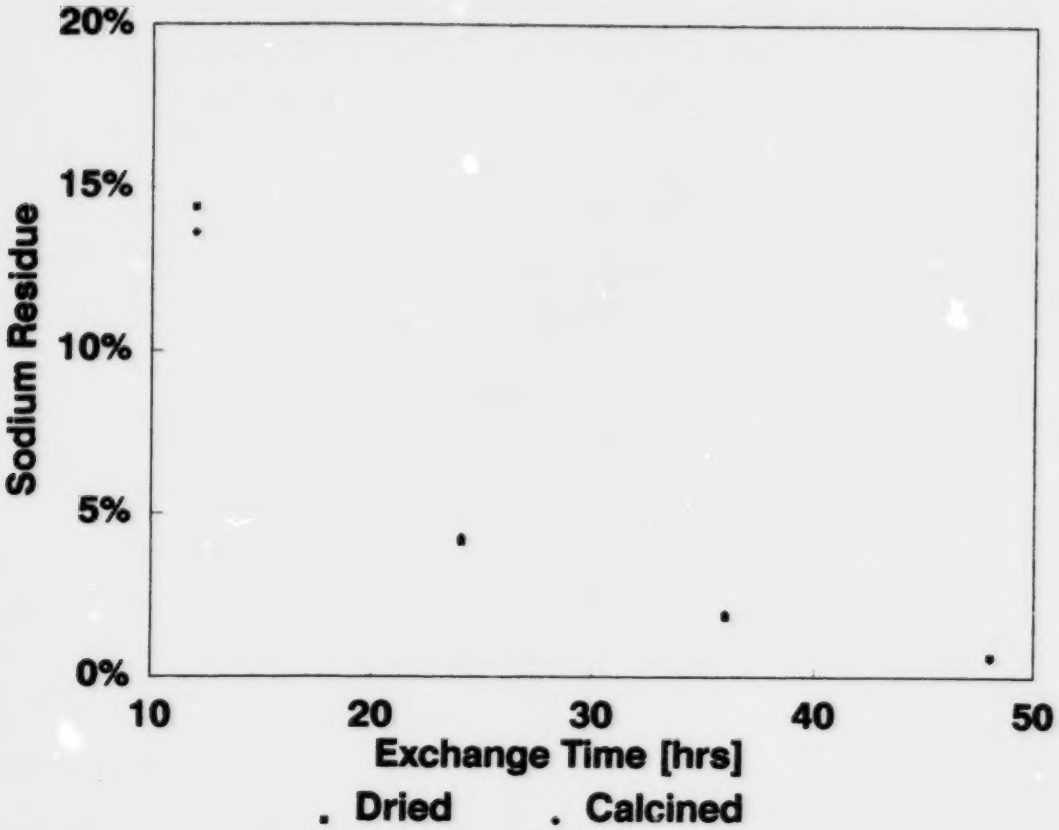


Fig. 4 The sodium residue in the Na NASICON precursor and the exchanged powders as calculated by the ratio method. Two types of powder are compared here: (a) exchanged powders which have been dried, and (b) exchanged powders which have been calcined.

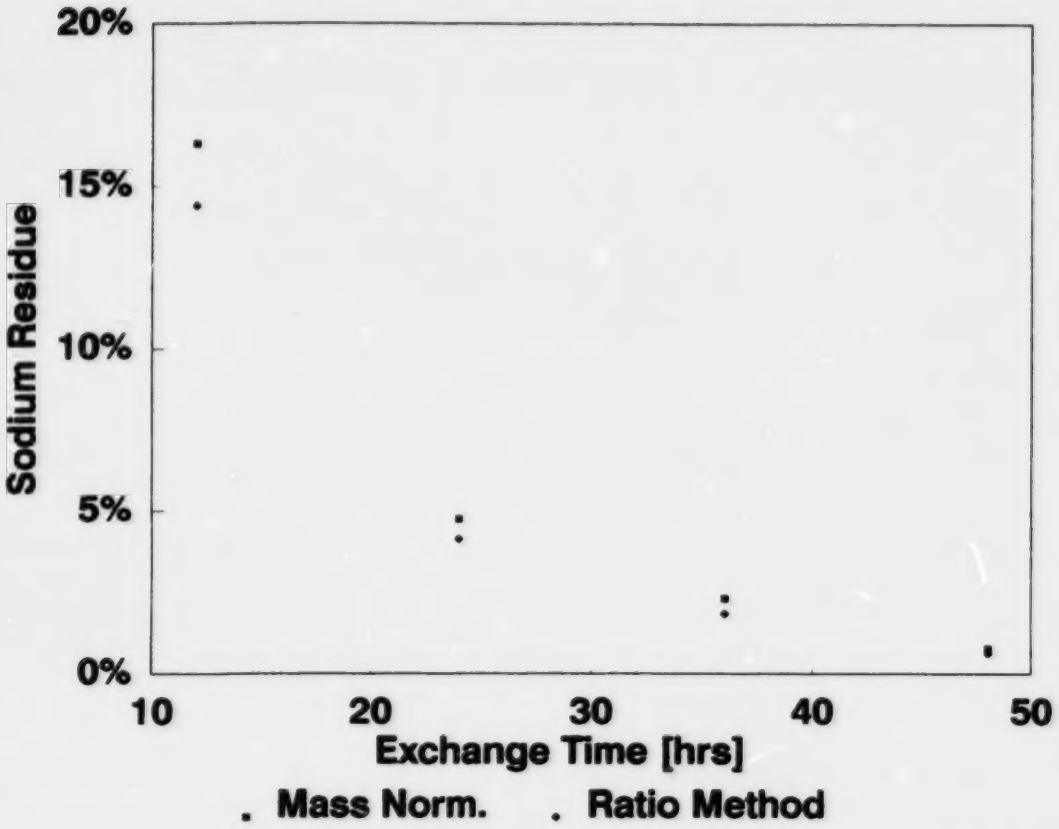


Fig. 5 A plot of sodium residue for the exchanged powders (dried) vs. number of ion exchange steps. The residues were obtained by both the mass normalization method and the ratio method. Note that the mass normalization method produces values that are slightly greater than the values obtained by the ratio method.

Examination of Fig. 5 disclosed that the mass normalization method produced values which are larger than those produced by the ratio method. In this case one must consider that the powder's mass changes as a result of the substitution of sodium (molecular weight = 23) with hydronium (molecular weight = 19). The complete exchange of NASICON would cause its molecular weight to fall from 520.5 to 510.5 amu: a decrease of 1.9%. This should cause a corresponding difference between the sodium residue calculated by the ratio method and that calculated by the mass normalization method. But the difference is too large to be accounted for by a change of powder density, there is the need to consider the possibility that some of the Na NASICON precursor decomposed during ion exchange.

Since there was a significant ^{97}Zr peak, one may determine the number of ^{97}Zr counts per mg of sample mass. An increase in the specific ^{97}Zr counts as sodium was removed from the samples was observed (Table 12). It was this phenomenon which provided an explanation of why there was an unexpected difference between the results of the mass normalization method and the ratio method.

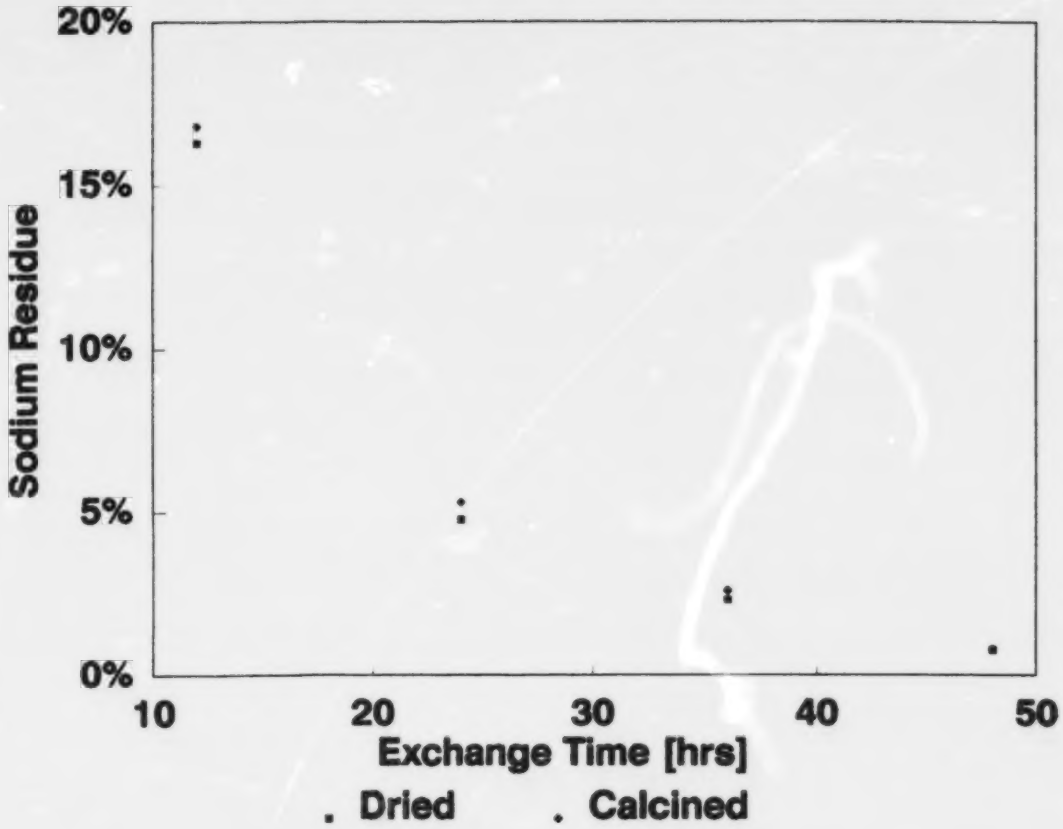


Fig. 6 The sodium residues in the Na NASICON precursor and the exchanged powders as calculated on the basis of the mass normalization method. There were two types of powder compared here: (a) exchanged powders which have been dried, and (b) exchanged powders which have been calcined.

5.2 Series Two

The second series of tests on the exchanged powders was performed in an attempt to examine the change in sodium residue (particularly "conducting" sodium) during the first stages of the exchange. Although the results did not yield this information, an improved understanding of the ion exchange process in NASICON was gained. The results for the ion exchanged powders are presented in tables and figures which follow.

Table 14 presents the $^{24}Na/mg$ values, $^{97}Zr/mg$ values, and the $^{24}Na/^{97}Zr$ ratios. The results for sample 30 (precursor) were consistent with the values obtained for the precursor during the study of the first series of powders (Table 12, page 33). As in the case of the first series, the $^{24}Na/mg$ values dropped rapidly during the first exchange step. In addition, the $^{97}Zr/mg$ values increased after the first exchange step. The sodium residues were calculated by both the mass normalization and ratio methods (Table 15).

Table 14 A tabulation of the specific activities of ^{24}Na, ^{97}Zr, and the $^{24}Na/^{97}Zr$ ratio for the second series of powders.

Sample Number	^{24}Na/mg	^{97}Zr/mg	$^{24}Na/^{97}Zr$
30	$6.4 \times 10^3 \pm 40$	129 ± 12	49.60 ± 4.63
31	$1.6 \times 10^3 \pm 20$	163 ± 8	7.43 ± 0.25
32	445. ± 4	165 ± 3	2.69 ± 0.06
33	224. ± 3	166 ± 2	1.47 ± 0.03
34	248. ± 3	179 ± 3	1.39 ± 0.03
35	112. ± 2	167 ± 2	0.67 ± 0.01
36	83. ± 1	161 ± 2	0.52 ± 0.01
37	86. ± 1	172 ± 2	0.50 ± 0.01

Table 15 A tabulation of sodium residues as determined by the mass normalization and ratio methods.

Sample Number	Sodium res. mass method [%]	Sodium res. ratio method [%]
30	100.0 ± 0.6	100.0
31	25.0 ± 1.6	15.0 ± 1.5
32	7.0 ± 0.4	5.42 ± 0.52
33	3.8 ± 0.3	2.96 ± 0.27
34	3.9 ± 0.3	2.79 ± 0.27
35	1.8 ± 0.1	1.36 ± 0.13
36	1.3 ± 0.1	1.04 ± 0.10
37	1.4 ± 0.1	1.01 ± 0.10

The sodium residues (ratio method) in Table 15 are plotted in Figs. 7 and 8 with the sodium residues calculated from the first series of experiments (Table 13, page 35).

In Fig. 7, there is no correspondence between the sodium residues for the first series and the second series when plotted with respect to exchange time. Upon closer examination of the two sets of results, it was determined that when the two curves were plotted with respect to exchange step, rather than the elapsed exchange time, a similarity became evident (Fig. 8).

One may conclude from this result that the NASICON/acid system proceeded to equilibrium rapidly, and a large fraction of the structural sodium was lost within the first half hour of the exchange process.

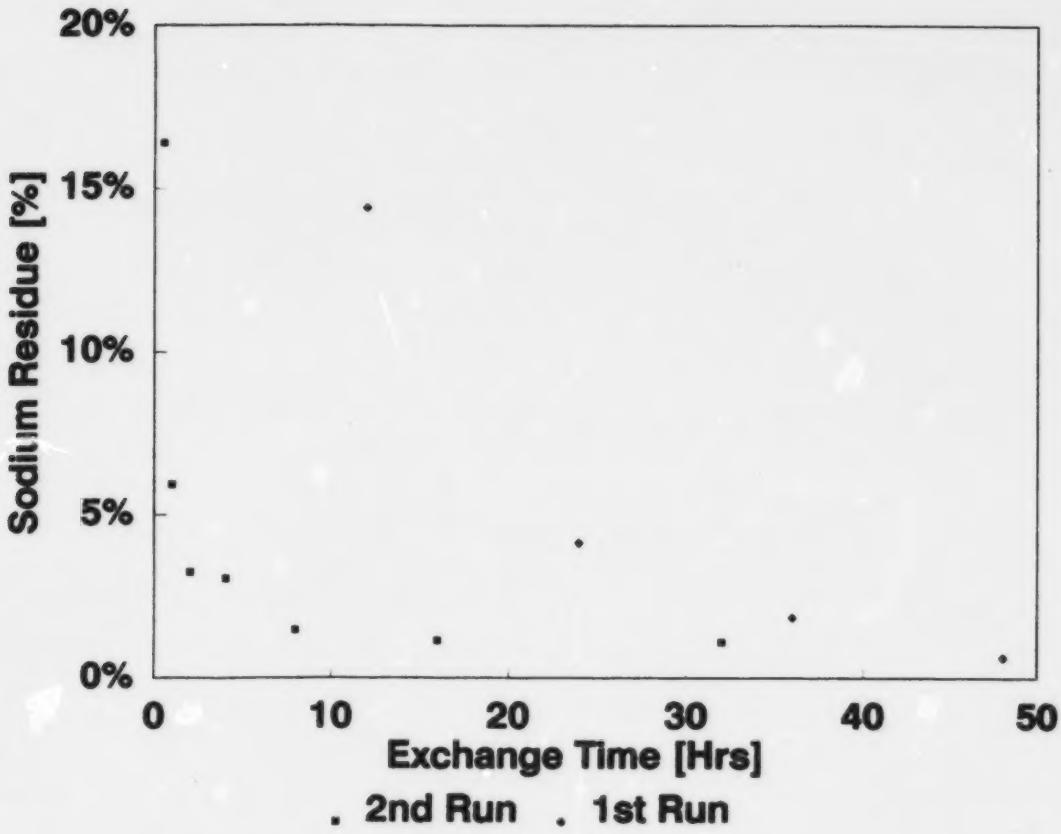


Fig. 7 The sodium residue for the NASICON powders of the first and second series plotted with respect to exchange time.

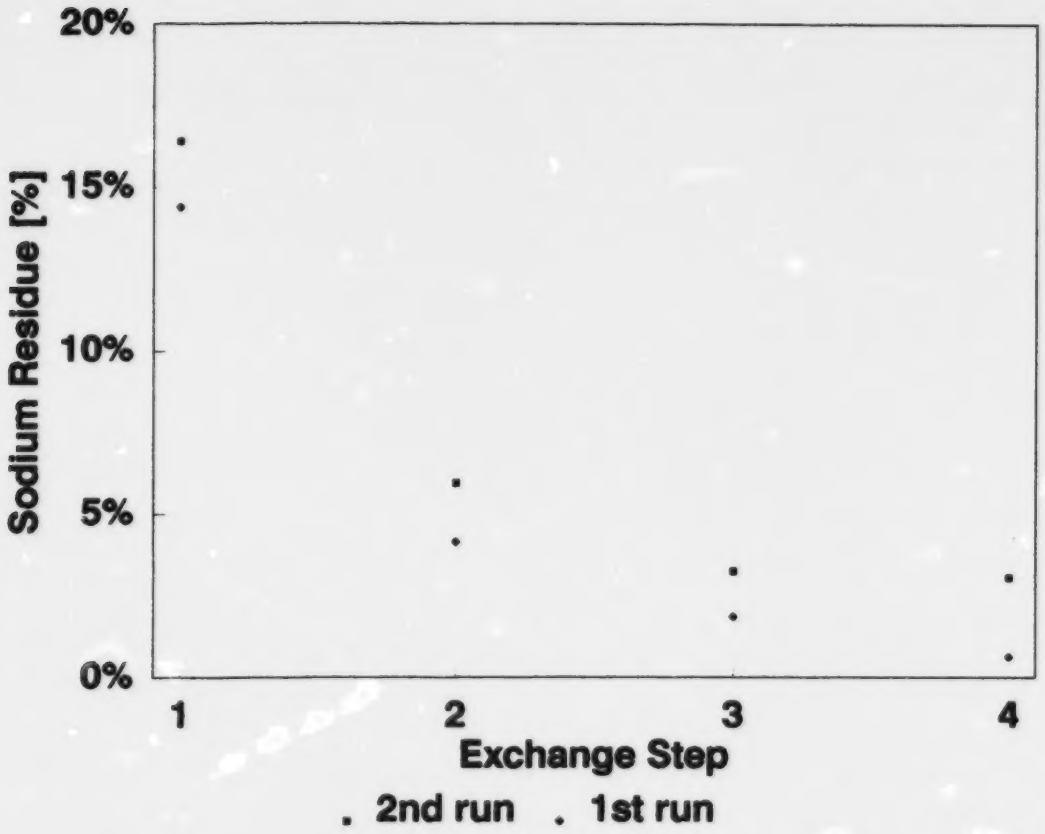


Fig. 8 The sodium residue for the NASICON powders of the first and second series plotted with respect to exchange step.

After each exchange step, a small quantity of the waste acid was retained for ICP analysis (Table 16). It was possible to provide independent confirmation of the sodium residues determined by INNA, and test the validity of the assumption that the zirconium content of the NASICON powder is not affected by the acid treatments.

The concentration of zirconium in each batch of waste acid was less than 1 mg/litre; this represented a negligible loss of zirconium from the NASICON (e.g. a loss of 150 ppm in the final exchange step - the worst case). The phosphorus and silicon loss also appeared to be negligible. Evidence of an aluminum contamination in the Na NASICON powder was also detected.

The amounts of sodium found in the waste acid accounted for the sodium loss from the NASICON powder as shown graphical in Fig. 9. Here, the accumulative sodium loss, as determined by ICP, is plotted with the sodium content of the NASICON powder (as determined by INNA). The fact that quantities of powder were retained after each exchange, and that there were losses of powder during the filtration process, was taken into account when preparing the chart.

Table 16 The concentration of sodium, zirconium, phosphorus, aluminum, and silicon in the waste acid solutions retained after each exchange step, as determined by ICP analysis.

Exchange Step	Concentration, mg/litre Na	Zr	P	Al	Si
1	1780	< 0.01	37	.22	5.7
2	196	0.05	2.8	0.54	1.7
3	61	0.33	1.5	0.56	2.0
4	29	0.18	0.8	0.94	2.6
5	15	0.20	0.5	1.7	4.1
6	8.3	0.19	< 0.5	1.6	6.6
7	7.3	0.31	< 0.5	1.8	9.5

Table 17 ICP analysis of NASICON ion-exchange solutions. For the second series of powders.

Time for acid ion-exchange (Hours)	Amount Determined in Acid Solution mg/g of NASICON Na	Zr	P	Si
0.5	89	< 0.001	1.9	0.29
1.0	10	0.002	0.15	0.09
2.0	3.4	0.018	0.08	0.11
4.0	1.7	0.011	0.05	0.15
8.0	0.94	0.012	0.03	0.26
16.0	0.55	0.012	< 0.03	0.44
32.0	0.52	0.022	< 0.03	0.68
TOTAL	106.1	0.077	2.2	2.02

For NASICON with x = 1.5

Total Na = 57.5 g/520.5 g NASICON
= 110 mg/g

Exchangeable Na = 34.5 g/520.5 g NASICON
= 66 mg/g

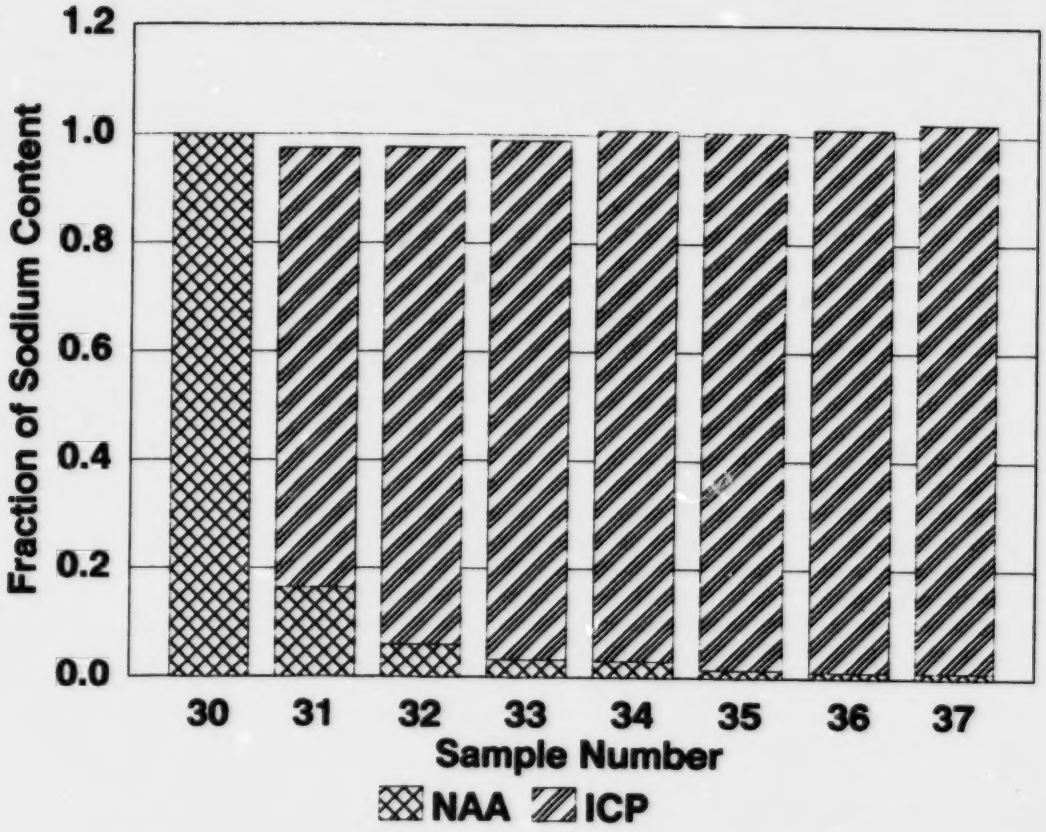


Fig. 9 A plot of sodium content of the NASICON powders and the waste acid at each stage of exchange. All values have been adjusted for the quantity of NASICON which had been exchanged at each step. The ICP results are accrued values.

Analysis of the second set of powders by X-ray fluorescence (Table 18) provided further support of the finding that much of the structural sodium was removed from the NASICON powder.

The weight fraction of Na_2O followed a decline similar to that predicted by the INNA and ICP analysis. After the first ion exchange step, the fraction of ZrO_2 increased by approximately 11%; subsequent ion exchange steps effected smaller increases in this fraction. Assuming that ZrO_2 was not being removed from the sample, the increase in its fraction indicated that the other oxides were being leached from the NASICON. By employing the ZrO_2 content as a normalization factor, it was revealed that both the silicon and phosphorus oxide contents of the powder were reduced by approximately 20%. This suggested that a fraction of Na NASICON had been destroyed during the exchange process, leaving behind ZrO_2 powder.

The fraction of ZrO_2, when represented as weight percent, made a marked increase after the first exchange step which indicated an increase in the mole fraction of zirconium in the sample. Although silicon and phosphorus were not measured by INNA, the increased concentration of zirconium was observed in the INNA results. When the zirconium contents for the powders were normalized with respect to the precursor's zirconium content, almost identical results were obtained by each method. Therefore one may rely on INNA for

an assessment of the quantity of NASICON remaining in the exchanged powder (Fig. 10).

Table 18 The results of the XRF analysis of the second series of NASICON powders. The units are weight percent.

Oxide:	ZrO_2	SiO_2	Al_2O_3	P_2O_5	Na_2O
Sample					
Precursor	45.5	19.8	0.60	21.6	13.2
1	56.4	19.7	0.64	20.7	2.7
2	57.0	19.9	0.55	21.1	1.3
3	56.9	20.3	0.60	21.5	0.39
4	58.0	20.0	0.52	21.2	0.71
5	57.7	20.2	0.62	21.2	0.69
6	58.9	19.4	0.46	20.7	0.16
7	59.1	19.6	0.51	20.6	0.14

Table 19 The quantities of ZrO_2, SiO_2, and P_2O_5 in the NASICON powder at each stage of exchange after renormalizing for just those oxides.

Oxide:	ZrO_2	SiO_2	P_2O_5
Sample			
Precursor	52.4	22.8	24.9
1	58.3	20.4	21.4
2	58.2	20.3	21.5
3	57.6	20.6	21.8
4	58.5	20.2	21.4
5	58.2	20.4	21.4
6	59.5	19.6	20.9
7	59.5	19.7	20.7

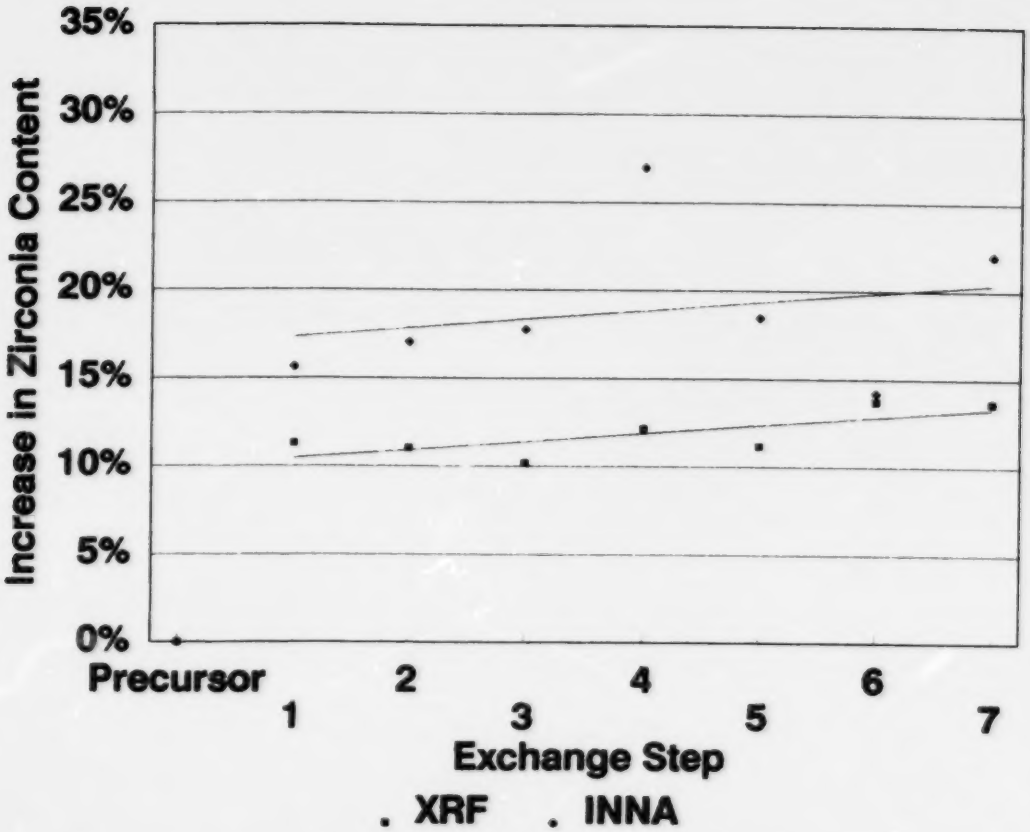


Fig. 10 The proportions of zirconium in the second series of powders as determined by XRF and INNA. The two lines represent a linear regression fit of each set of data, only the data points corresponding to the precursors were excluded.

It is important to consider that the amount of ZrO_2 found in the powder gives only an estimate of the fraction of Na NASICON precursor which decomposed during the acid treatment; it was likely that unknown amounts of ZrO_2 were lost during the filtration process and remained undetected by ICP analysis. The estimate of the weight fraction of ZrO_2 present in the powder is the relevant quantity to determine since the Hyceram pellets will contain this oxide.

5.3 XRD Results

The analysis of the crystal structure of Hydronium NASICON was of great importance to this study since it was necessary to confirm weather or not the Hydronium NASICON was rhombohedral like its Na NASICON precursor. The XRD patterns obtained at CANMET were confirmed through additional analysis at Whiteshell. Both sets of data exhibited small zero angle and/or sample displacement error. The correction of these errors was made at Whiteshell by making use of two pairs of related reflections: 012/024 and 110/200, which have precise d-spacing ratios of 2 and $\sqrt{3}$ respectively. The empirical 2θ corrections were found to be 0.13° (Whiteshell data on precursor) and 0.09° (CANMET data on Hydronium NASICON).

The analysis proceeded without a further modification of the data which would not be justified without more precise 2θ corrections of the type obtained through the use of internal standards such as Si powder. The quality of the

data was sufficient to permit the conclusion to be drawn that the Na NASICON precursor and the final product, Hydronium NASICON, both have the rhombohedral crystal structure.

The intermediate stages of exchanged material were distinct from the precursor or final product in that there was a deviation from the rhombohedral symmetry. Furthermore, a widening of the features was strongly evident in the XRD plots for the intermediate powders. Unfortunately, the use of powder diffraction methods made it difficult to precisely establish the nature of the deviation. But consideration may be given to the possibility that a mixture of Hydronium ions (effective radius 1.43 Å) and sodium ions (ionic radius 0.98 Å) with their mismatched radii are the source of microscopic lattice stress and distortion. The sequence of XRD patterns shows that the final phase (Hydronium NASICON) increases in quantity as the intermediate phase diminishes; there is no evidence of the intermediate phase in the final product.

The indexing of the precursor and Hydronium NASICON was based upon an earlier work [13] in which an indexing of $Na_3Zr_2Si_2PO_{12}$ had been reported for NASICON above its transformation temperature, in the rhombohedral form. The hkl indices were required to satisfy the condition, $-h + k + l = 3n$, where n are integers.

The results of the indexing are presented in Table 20 for both the precursor (Na NASICON) and the final product (Hydronium NASICON). Any features in this work which were

not reported in the other work [13], are marked with an asterisk. In the case of Hydronium NASICON, a couple of features appeared to be a superposition of two sets of adjacent indices; these are denoted with brace brackets. There are three features indicated in Table 20 which are suspected to arise from the presence of monoclinic zirconia. The indices, 211 and 122, could be due to the superposition of features arising from zirconia and NASICON.

The INAA and XRF work demonstrated the presence of free zirconia in the partially and fully exchanged samples. Therefore the occurrence of features attributed to zirconia is not surprising. The lack of strong zirconia features in the Hydronium NASICON may be a consequence of the free zirconia having a very small grain size.

The C-axis increased in length by approximately 5%, and the A-axis decreased in length by approximately 2% as a result of the substitution of sodium with hydronium. The lattice parameters for the Na NASICON precursor were calculated to be: $a = 8.98_2 \pm 0.01$ Å and $c = 22.93 \pm 0.02$ Å. Those for the Hydronium NASICON product were calculated to be: $a = 8.79_0 \pm 0.01$ Å and $c = 24.14 \pm 0.02$ Å. These parameters, and the manner in which they changed as a result of ion exchange, were consistent with other lattice parameters reported for Na NASICON and its exchanged products [13, 12]. One may conclude that the final product of the ion exchange sequence is truly Hydronium NASICON.

table 20 X-ray diffraction data for precursor material and fully exchanged material. The initial indexing was based on previous work on $Na_3Zr_2Si_2PO_{12}$; an asterisk, *, indicates a diffraction feature which was not reported [13].

	Na NASICON			Hydronium NASICON			
hkl	d_{obs} [Å]	d_{calc} [Å]	I/I_o	d_{obs} [Å]	d_{calc} [Å]	I/I_o	
012	6.435	6.437	42	6.439	6.439	38	
104	4.616	4.615	92	4.731	4.729	56	
110	4.491	4.491	92	4.394	4.395	86	
113	3.873	3.872	72	3.857	3.857	84	
*202?	3.676	3.683	3				
024	3.218	3.219	66	3.219	3.219	60	
	3.155		4	3.152		5	IrO_2?
	2.995$^{\alpha}$		6				
116	2.913	2.911	100	2.967	2.968	100	
*211				2.856	2.857	9	+IrO_2?
*122	2.847	2.848	5				+IrO_2?
*018	2.688	2.689	3	2.804	2.805	2	
214	2.616	2.616	31	2.598	2.597	15	
300	2.593	2.593	53	2.538	2.537	32	
125	2.477	2.475	2	2.473	2.472	1	
208	2.308	2.307	6	2.364	2.365	2	
220	2.246	2.246	4	2.197	2.197	5	
119	2.214	2.216	4				
				2.294$^{\beta}$	2.289 / 2.301	4	
*1.0.10?	2.201	2.199	5				
217	2.186	2.188	5				
*223	2.155	2.155	10	2.119	2.120	3	
306	2.145	2.146	9	2.147	2.146	15	
312	2.121	2.120	5				
				2.081$^{\beta}$	2.080 / 2.082	8	
128	2.052	2.052	13				
134	2.019	2.019	23	1.992	1.993	14	
0.2.10	1.974	1.975	10	2.039	2.039	10	
*0.0.12				2.015	2.012	3	
226	1.936	1.936	33	1.930	1.929	29	
042	1.918	1.917	7	1.879	1.880	4	
404	1.839	1.842	3	1.816	1.815	2	
*2.1.10	1.808	1.808	22	1.851	1.849	25	
137	1.800	1.802	10	1.801	1.801	5	
318	1.722	1.724	5	1.731	1.730	4	
*324	1.703	1.704	16	1.678	1.677	12	
410	1.697	1.698	25	1.661	1.661	19	
235	1.664	1.663	3	1.642	1.642	2	
*413	1.657	1.657	3				

α Broad Feature. Index may be either 107 or 205.

β Index is thought to be a superposition of adjacent indexes.

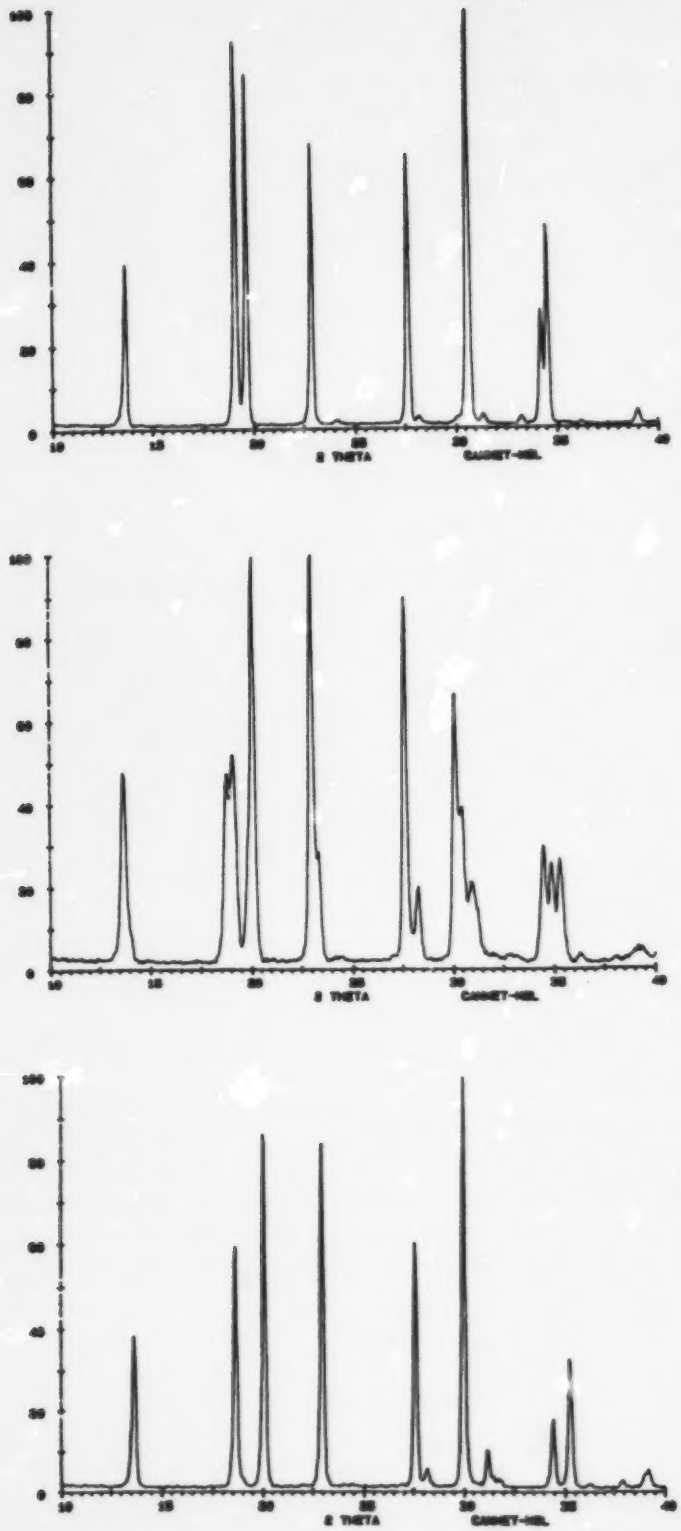


Fig. 11 The XRD patterns for the Na NASICON precursor (a), a sample subjected to three exchange steps (b), and the fully exchanged product (c).

5.4 Series Three

To test the validity of using the Na NASICON precursor as a standard, three types of Na NASICON powder (x = 0, x = 1.5, and x = 2.0) were tested with respect to NaCl and Na_2CO_3 standards previously tested at SLOWPOKE. By using such standards, it was also possible to determine the sodium content of the precursors in weight percent (Fig. 12). The stoichiometric sodium contents are shown for comparison (Table 21). From these results, one may conclude that the Na NASICON precursors had been produced with the correct sodium content, and can serve as suitable standards for the INAA work.

Table 21 A listing of the experimentally (INAA) and the stoichiometrically determined sodium compositions for three types of Na NASICON: x = 0, 1.5, and 2.

x value	Sodium Content (wt/o)	
	INAA	Stoichometric
0	4.52	4.24
1.5	10.66	10.61
2	12.60	12.73

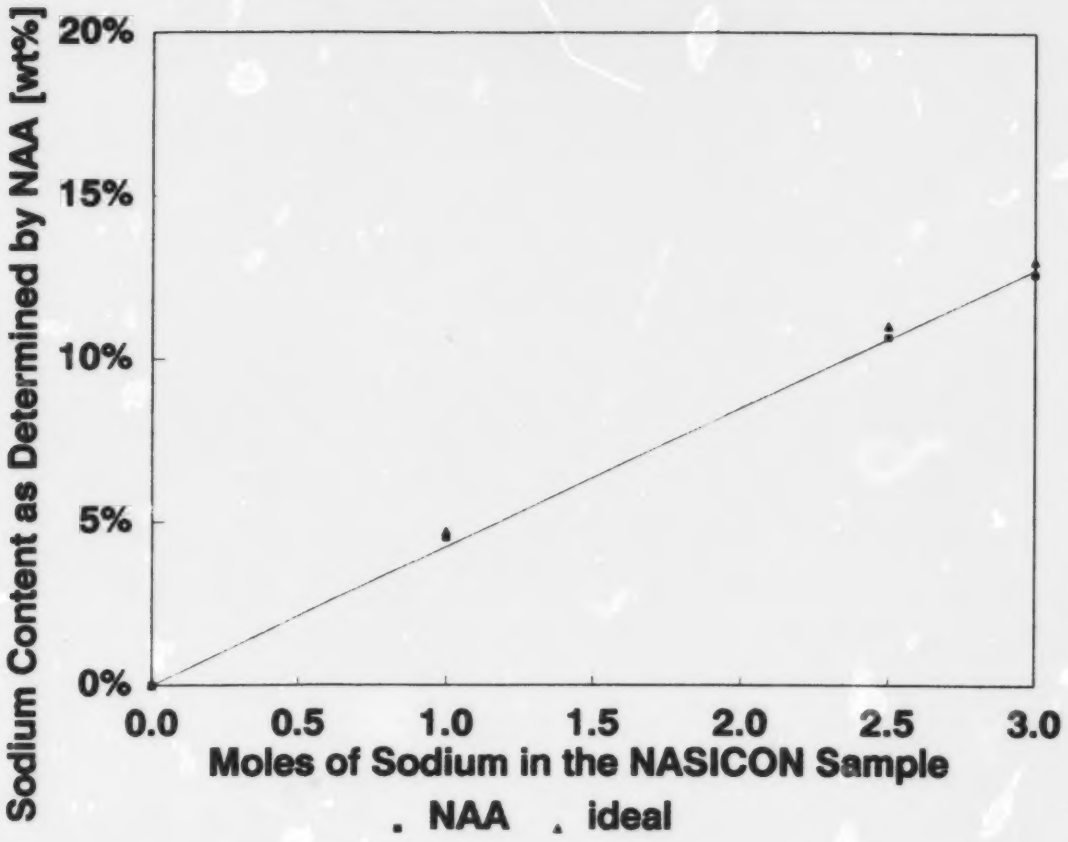


Fig. 12 The weight percent sodium content of three precursors (x = 0, x = 1.5, x = 2.0) with respect to the sodium content in moles.

5.5 Discussion of the Ion Exchange of NASICON Powders

It was originally expected that the sodium ions occupying the structural sodium sites (N1) would not have been displaced from their lattice sites by the hydronium ions. The sodium ions occupying the N1 sites are at a lower potential than those in the conducting sites (N2) by ~0.3 eV.

The INAA results showed that in addition to the removal of the N2 sodium, most of the N1 sodium was also being lost. XRF analysis of the powders and ICP analysis of the waste acid confirmed the discovery.

The results of tests on the second series of powders showed that most (~80%) of the sodium was lost within the first half hour of exchange. Therefore a very fast ion exchange reaction was evident.

The XRF tests showed that approximately equal amounts of silicon and phosphorus oxides were being removed from the sample. Furthermore, INAA and XRF results showed that zirconia remained in the sample. The mechanism which allowed the zirconia to remain was not known. It could be speculated that the particles of zirconia adhere to the surface of the NASICON granules.

The XRD work showed that the crystal structure of Hydronium NASICON was rhombohedral (as was the case for the Na NASICON precursor). Therefore it was evident that there was no change in the crystal structure of the NASICON powder as a result of replacing the sodium ions with the larger Hydronium ions. But the presence of small quantities of residual

sodium was found to cause a distortion of the lattice which might have arisen from stresses caused by the presence of the smaller sodium ions distributed throughout a lattice dominated by the larger hydronium ions. There did not appear to be a simple linear relationship between the amount of distortion present and the sodium residue.

The XRD results also suggested that the extra quantity of zirconia was in the form of a fine powder (finer than the NASICON powder). The process of bonding the Hydronium NASICON into pellets might be aided by the presence of the extra zirconia.

6 Study of Beta Alumina

6.1 Introduction

Although the study of NASICON was the main objective of this work, analysis of β" Alumina was performed as a test of the method of analysis used to study the ion exchange of the NASICON.

Since NASICON contains both structural (N1) and conducting (N2) sodium, virtually complete removal of the sodium as a result of relatively mild acid treatments at moderate temperatures (as opposed to treatment in molten nitrates [12]) was expected. The testing β" Alumina powder was performed because there was interest in confirming the presence of non-labile sodium in a fine powder of β" Alumina.

The ion exchange behaviour of ß" alumina is believed to be different from that of ß alumina [15]. The ion exchange of ß alumina in either molten $AgNO_3$ or KNO_3 may proceed to completion. But it was found that when ß" alumina was ion exchanged in a similar way, it contained a fraction of non-labile sodium equal to approximately 13% to 16% of the original quantity of sodium. Since polycrystalline ß" alumina samples had been used, there was concern that the unexchangeable sodium had become trapped at the grain boundaries in a second phase. Although X-ray micro-analysis disclosed the presence of a second phase which was less exchanged than the ß" alumina, there was not a sufficiently large quantity of it to account for the amount of unexchanged sodium in the sample.

6.2 Sample Preparation

The ß" Alumina powder (MgO doped) was prepared at CANMET for the test. They performed the ion exchange steps in 0.2 M HCl solution at 90°C on the same schedule as the series two NASICON powders (Table 23).

When performing the INAA studies, there was concern that a fast neutron reaction with ^{27}Al would produce sufficient quantities of ^{24}Na to cause significant errors in the estimates of sodium residue in the ß" Alumina powders, viz $^{27}Al(n,\alpha)^{24}Na$. Furthermore, it was discovered during the XRF tests of the NASICON powders that a small quantity (~0.5 wt%) of Al_2O_3 contaminant was present in all samples.

To assess the magnitude of the fast reaction's contribution to the sodium measurements, the sodium content of irradiated aluminum wire was measured (Fig. 13, page 64).

Table 22 The aluminum metal samples. Type 1100 aluminum metal wire was used.

Sample number	Mass [mg]	Brief Description
20	84.7	All samples (20 to 23) are in the form of metallic aluminum.
21	169.2	
22	253.5	
23	532.3	

Table 23 Samples of ß/ß" alumina powder.

Sample number	Mass [mg] a	b	Brief Description
40	91.6	74.9	ß/ß" alumina powder. Used as precursor for this exchange series.
41	137.0	127.4	Exchanged once, 30 minutes. 0.2 M HCl.
42	156.9	142.2	Exchanged twice, total 1 hour. 0.2 M HCl.
43	151.1	181.6	Exchanged three times, total 2 hours. 0.2 M HCl.
44	142.5	86.9	Exchanged four times, total 4 hours. 0.2 M HCl.
45	147.5	107.1	Exchanged five times, total 8 hours. 0.2 M HCl.
46	224.7	178.0	Exchanged six times, total 16 hours. 0.2 M HCl.
47	128.3	234.5	Exchanged seven times, total 32 hours. 0.2 M HCl.

6.3 Results

A linear relationship between sample mass and the total number of ^{24}Na counts was observed (Fig. 13); the slope of the line determined the number of ^{24}Na counts per gram of aluminum (in the sample) which would be measured from a specimen irradiated for 5 minutes at 5 Kwatts power. The value of the slope was found to be 14.5 ± 0.3 ^{24}Na counts per mg of aluminum.

The aluminum content of ß" Alumina is approximately 50 wt %. It was on this basis that a small correction was made to the ^{24}Na measurements made on the ß" Alumina samples (Table 24).

Table 25 lists the sodium residues for the ß" Alumina samples as calculated from the INAA and XRF results. The INAA results appear to have less scatter than the XRF results, particularly at lower sodium residues.

Fig. 14 shows a plot of sodium residue (INAA) with respect to ion exchange time. There appears to be a leveling off of sodium residue at a value of approximately 10%.

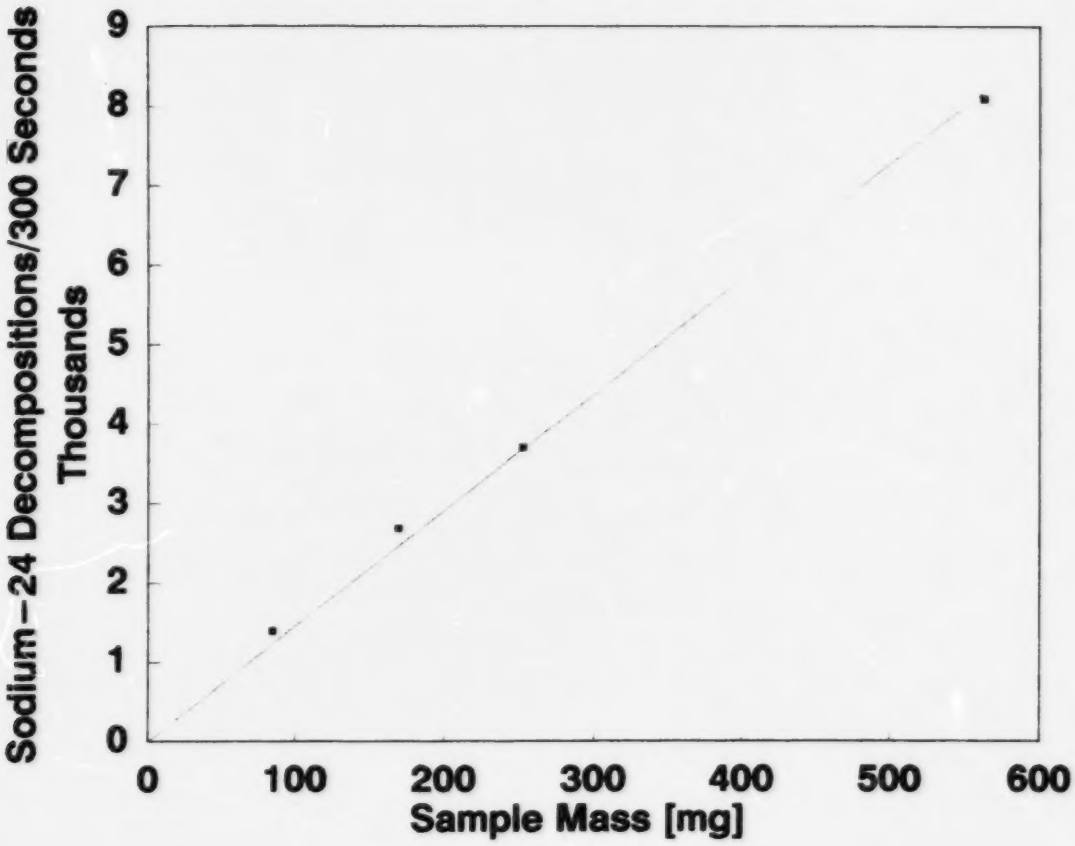


Fig. 13 A plot of ^{24}Na decompositions per 300 seconds for aluminum metal exposed to the neutron flux of the SLOWPOKE at 5 Kwatts power. The activities are adjusted for delay and position zero.

Table 24 The number of ^{24}Na counts per mg of β" alumina powder irradiated at 5 Kwatts for 300 seconds and counted for 300 seconds. Since two different counters were used, the correction factors for the fast neutron production of ^{24}Na were adjusted accordingly.

Sample number	Exchange Time [hrs]	a		b	
		meas.	corr.	meas.	corr.
40	0.0	268	264	424	416
41	0.5	55	50	89	81
42	1.0	49	44	75	68
43	2.0	42	38	66	58
44	4.0	42	37	-	-
45	8.0	38	33	55	48
46	16.0	35	30	54	47
47	32.0	31	26	49	42

Table 25 The sodium residues with respect to ion exchange time calculated for the β" Alumina samples. Both INAA and XRF were used.

Exchange Time [hrs]	INAA	XRF
0.5	19.2%	20.7%
1.0	16.5	18.1
2.0	14.2	16.5
4.0	14.0	15.1
8.0	12.0	15.6
16.0	11.3	17.2
32.0	9.9	14.1

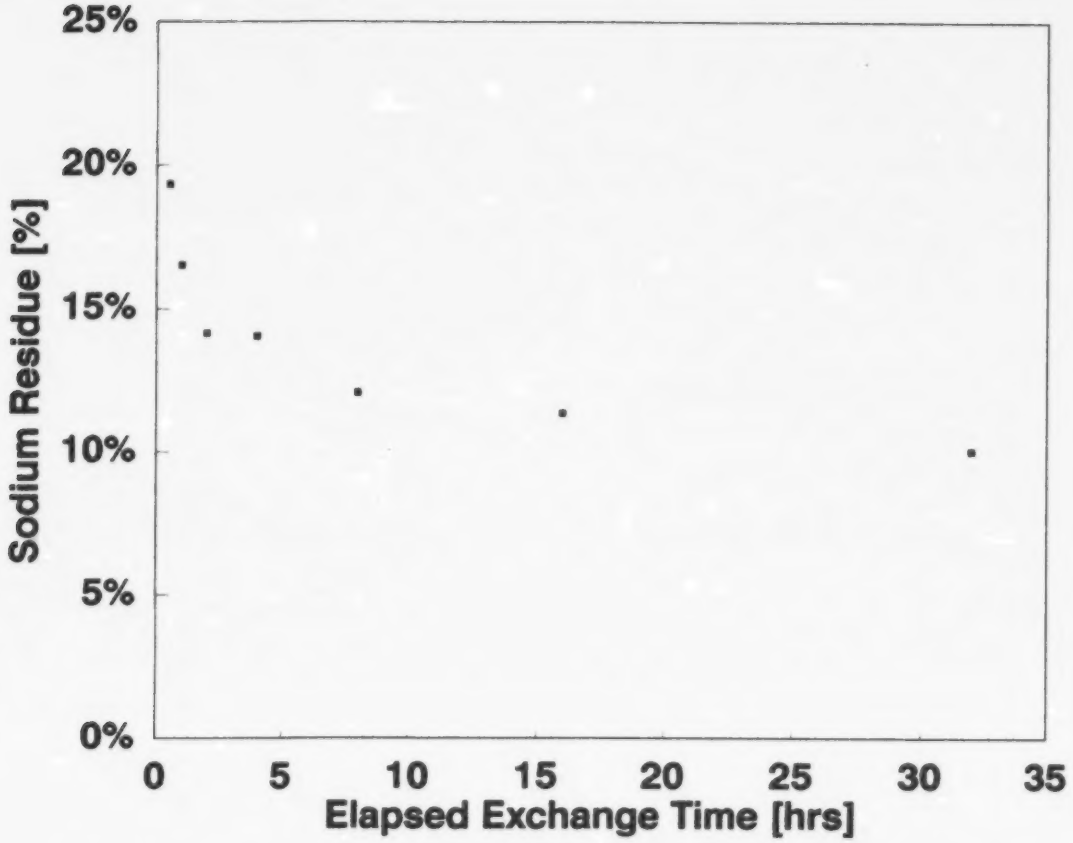


Fig. 14 The sodium residue in ß" Alumina powder as a function of exchange time.

6.4 Discussion of the Results of Testing β" Alumina

Although the corrections made to the values in Table 24 were small, the corrected values were used for calculating the sodium residues (Fig. 14). It was reasonable to assume that no correction was necessary for the sodium residues calculated for the NASICON powders since the aluminum contamination was small.

Approximately 10% of the sodium in the β" Alumina samples was not exchanged from the material. Such an amount of non-labile sodium is consistent with the results of ion exchange measurements performed on polycrystalline samples of β" Alumina where 13 to 16% of the sodium was found to be unexchangeable. It is important to realize that the β" Alumina which was ion exchanged for this study was in the form of a powder rather than relatively large polycrystalline samples. Therefore the existence of non-labile sodium was confirmed, and one may conclude that the β" Alumina samples display the ion exchange characteristics which had originally been expected for NASICON.

7 The Analysis of the Pellets

7.1 Thermal Neutron Flux

The same INAA technique was used for the measurement of residual sodium in the Hyceram pellets. Since the pellets were composed of Hydronium NASICON bonded with phosphoric acid, the additional material increased the sample mass which diluted the sodium and zirconium.

Estimates of sodium residue were made on the basis of the ratio method and the mass normalization method. Some pellets were also analysed by X-ray fluorescence to corroborate the results obtained by INAA.

The standard $^{24}Na/^{97}Zr$ ratio used for the pellets was the same as that used for the exchanged powders: 45.3 ± 2.1. This is justified since the gamma ray absorption by the samples is small and the use of the ratio method removes the effect of mass dilution. Table 26 shows the $^{24}Na/^{97}Zr$ ratios for the Hyceram samples, along with the calculated sodium residues.

The Hy100 through Hy300 series pellets are composed of powders which underwent a single exchange. Several batches of exchanged powder were prepared for these series; this is evident in the fluctuations in the sodium residues. The Hy400 series pellets were more extensively exchanged, consequently the sodium residues are significantly lower than those in the previous series. The three Hy400 series pellets appear to have been manufactured from two separate batches of exchanged powder.

The sodium residues were also calculated on the basis of the mass normalization method. Table 27 shows the number of ^{24}Na counts per mg of sample mass with the sodium residues calculated on the basis of the mass normalization method.

Table 26 The $^{24}Na/^{97}Zr$ ratios for the Na NASICON precursor and the Hyceram pellets. The sodium residues were determined from these values.

Sample number	$^{24}Na/^{97}Zr$ ratio	Sodium residue (ratio method)
1 and 2	45.3 ± 2.1	100 ± 4.6
Hy146	4.35 ± 0.09	9.59 ± 0.32
Hy206	2.22 ± 0.05	4.89 ± 0.28
Hy231	2.75 ± 0.06	6.07 ± 0.24
Hy288	8.98 ± 0.24	19.8 ± 0.64
Hy319	3.46 ± 0.08	7.64 ± 0.30
Hy328	3.47 ± 0.09	7.66 ± 0.31
Hy347	3.40 ± 0.07	7.51 ± 0.25
Hy392	4.27 ± 0.10	9.43 ± 0.38
Hy393	4.14 ± 0.08	9.14 ± 0.35
Hy396	4.22 ± 0.10	9.30 ± 0.37
Hy471	1.02 ± 0.03	2.24 ± 0.07
Hy477	0.61 ± 0.02	1.34 ± 0.05
Hy486	0.59 ± 0.02	1.30 ± 0.06

Table 27 The ^{24}Na counts per mg of sample mass for the Na NASICON precursor and the Hyceram pellets. The sodium residues calculated on the basis of the mass normalization method are included.

Sample number	^{24}Na/mg	Sodium residue
1 and 2	$6.3 \times 10^3 \pm 20$	100.0 ± 0.4
Hy146	533 ± 4	8.41 ± 0.07
Hy206	270 ± 3	4.26 ± 0.05
Hy231	327 ± 3	5.16 ± 0.06
Hy288	$1.13 \times 10^3 \pm 10$	17.9 ± 0.1
Hy319	446 ± 4	7.05 ± 0.07
Hy328	424 ± 4	6.69 ± 0.07
Hy347	441 ± 4	6.96 ± 0.06
Hy392	539 ± 5	8.51 ± 0.08
Hy393	535 ± 4	8.44 ± 0.07
Hy396	525 ± 5	8.30 ± 0.08
Hy471	136 ± 3	2.14 ± 0.04
Hy477	77.5 ± 1.6	1.22 ± 0.03
Hy486	75.9 ± 1.9	1.20 ± 0.03

The sodium residues calculated by the mass normalization method are noticeably lower than those calculated by the ratio method (Fig. 15). This is a result of the mass dilution effect which arises from the addition of phosphoric acid during the bonding process.

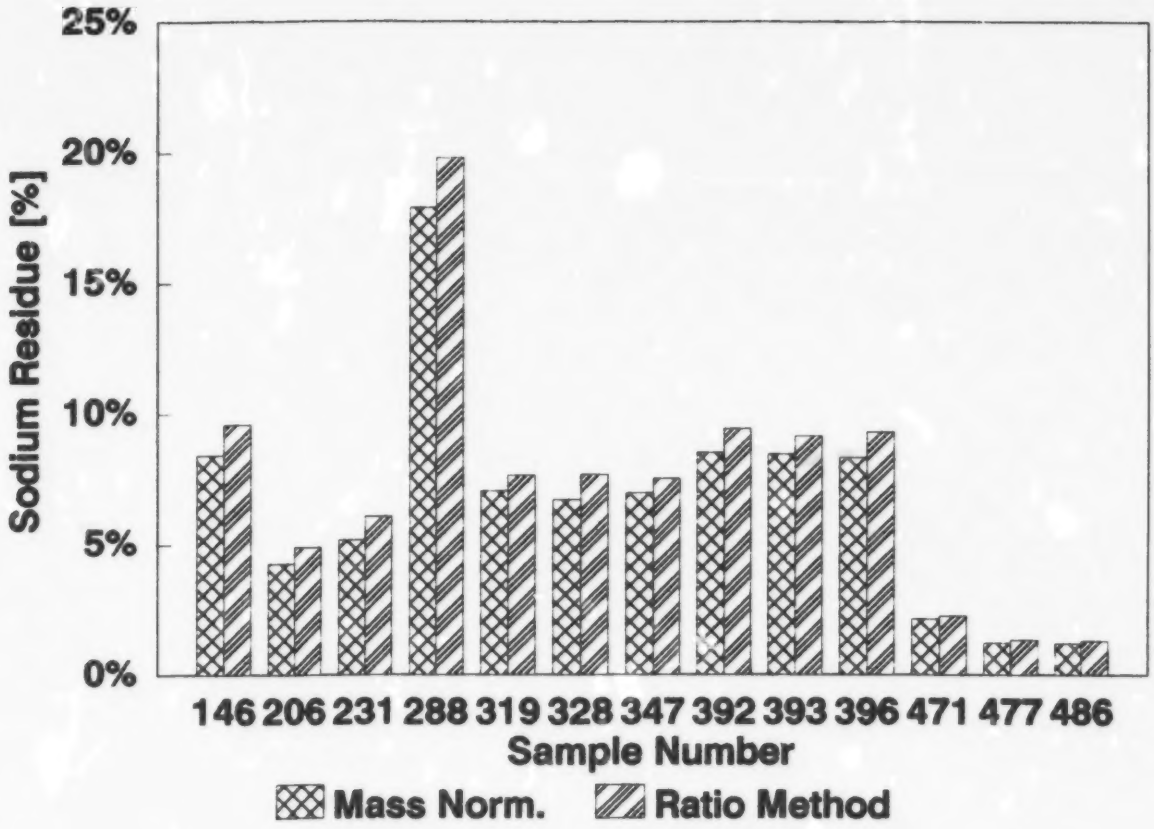


Fig. 15 A bar graph of the residual sodium levels in the pellets of Hyceram. Take note of the fact that the sodium residues calculated on the basis of mass are considerably lower than the sodium residues calculated by the ratio method. This arises from the fact that the Hyceram is bonded with phosphoric acid, which provides an additional mass to the sample.

Note that the pellets of the first three series (i.e. the Hy100, Hy200, and Hy300 series) are made of Hydronium NASICON powder which has been exchanged only once. The average sodium residue (ratio method) for the Hyceram pellets of these three series was calculated to be 9%; therefore, one may use 9% as an approximation of the sodium residue level in the first powders produced by CANMET.

The waste acid solutions (Table 2, page 7) of the five additional exchange steps performed on the early Hydronium NASICON samples at the Chalk River Nuclear Laboratories [10], provided an independent estimate of the amount of residual sodium in these first powders. Assuming that for each acid concentration the five exchange steps were sufficient to remove all remaining sodium, the average of the four total sodium masses, 12 mg, yielded an estimate of the sodium content of the powder. Since there was initially 110 mg of sodium in the one gram of Na NASICON precursor, the sodium residue is calculated to be approximately 11%, a result consistent with the INAA results, which suggest a sodium residue of approximately 9%.

7.2 Fast Neutron Flux

Fast neutron reactions are potentially useful in measuring the quantities of silicon and phosphorus in the NASICON powders and the Hyceram pellets. The possibility of determining the amount of additional phosphorus in the Hyceram was explored.

Table 4 (page 9) is repeated as Table 28 in order to facilitate a review of the nuclear reactions expected to occur when the NASICON is exposed to an epithermal flux.

Table 28 The nuclear reactions responsible for the creation of ^{28}Al and ^{29}Al [1].

	REACTION	DECAY CHARACTERISTICS OF THE PRODUCT: GAMMA RAY ENERGY [keV]	HALF LIFE
i	$^{29}Si + n \rightarrow {}^{29}Al + p$	1273	6.5 m
ii	$^{28}Si + n \rightarrow {}^{28}Al + p$	1779	2.24 m
iii	$^{31}P + n \rightarrow {}^{28}Al + \alpha$	1779	2.24 m
iv	$^{27}Al + n \rightarrow {}^{28}Al$	1779	2.24 m

These reactions occur in the SLOWPOKE reactor because approximately 5% of the total flux is composed of neutrons in the epithermal energy range. The very large release of gamma-rays from the decay of ^{24}Na made the measurement of the peaks associated with the decay of ^{28}Al and ^{29}Al isotopes difficult. An additional problem arose from the activation of ^{27}Al contaminant in the sample to produce ^{28}Al.

The production of ^{28}Al (reaction iv) was reduced by surrounding the sample with cadmium foil. The foil removed almost all of the thermal neutron flux thus reducing the amount of ^{28}Al produced from the activation of ^{27}Al. There is still some ^{28}Al arising from reaction iv since ^{27}Al has a resonance integral, I, equal to 0.17 b as compared to a thermal neutron capture cross-section, σ, of 0.233 b (Table 3, page 8).

The Cd shielded samples were irradiated at 5 kW power for 300 seconds. Upon removal from the SLOWPOKE reactor, as short a waiting time as possible transpired, (i.e. 2 to 3 minutes for most samples, 7 minutes for a solitary sample as a result of technical difficulties).

Since the half lives of the neutron activation products are considerably shorter than those for ^{24}Na and ^{97}Zr, it was necessary to account for the decay of ^{28}Al and ^{29}Al during the time which had passed since the sample was removed from the reactor. To do this the following equation was used.

$$|A|_0 = |A|_t \text{ X } EXP((t \text{ X } \ln(2)/t_{\frac{1}{2}}) \qquad (13)$$

$|A|_0$ is the number of counts for the nuclide, A, where the counting period starts at the time the sample emerges from the reactor. $|A|_t$ is the number of counts for the nuclide where the counting period starts at a time t minutes after the removal of the sample from the reactor; and $t_{\frac{1}{2}}$ is the half life of nuclide in minutes.

For ^{28}Al and ^{29}Al, the correction was made using these two specific forms of the previous equation.

$$|^{28}Al|_0 = |^{28}Al|_t \text{ X } EXP((t \text{ X } \ln(2))/2.24)) \qquad (14)$$

$$|^{29}Al|_0 = |^{29}Al|_t \text{ X } EXP((t \text{ X } \ln(2))/6.5)) \qquad (15)$$

where 2.24 is the half life of ^{28}Al in minutes, and 6.5 is the half life of ^{29}Al in minutes.

One Na NASICON sample and several Hyceram pellets were irradiated in Cd foil. Table 29 lists the sample numbers, the delay times, and the corresponding correction factors.

Table 29 The samples irradiated at 5 kw power in Cd foil. The delay times and correction factors are tabulated. Sample masses are included.

sample number	sample mass [mg]	delay time [min]	correction factors ^{28}Al	^{29}Al
1c	17.3	7.0	8.73	2.11
Hy146a	88.2	4.0	3.45	1.53
Hy146b	63.8	1.9	1.80	1.22
Hy288a	63.5	5.5	5.48	1.80
Hy288b	55.4	2.0	1.86	1.24
Hy347a	70.1	6.0	6.40	1.90
Hy347b	64.9	2.0	1.86	1.24
Hy471a	48.9	2.0	1.86	1.24
Hy471b	40.4	2.0	1.86	1.24
Hy477a	72.2	3.0	2.53	1.38
Hy477b	70.9	2.0	1.86	1.24

The correction factors were used to compensate for the decay of ^{28}Al and ^{29}Al after the sample has been removed from the reactor. These data were used to determine the values listed in Table 30: the specific activities of ^{97}Zr, ^{24}Na, ^{28}Al, and ^{29}Al.

Table 30 The specific activities of ^{97}Zr, ^{24}Na, ^{28}Al, and ^{29}Al.

sample number	^{97}Zr/mg	^{24}Na/mg	^{28}Al/mg	^{29}Al/mg
1c	139	253	686	13.2
Hy146a	117	24.5	917	18.6
Hy146b	119	26.6	888	17.7
Hy288a	144	58.3	919	13.0
Hy288b	129	54.3	840	12.9
Hy347a	127	21.5	1.04×10^3	19.3
Hy347b	115	20.2	928	16.0
Hy471a	121	7.77	943	20.1
Hy471b	131	7.59	1.03×10^3	19.3
Hy477a	117	5.72	908	14.1
Hy477b	118	5.01	909	16.4

Note that when compared to the results obtained from irradiations performed with no Cd foil (Table 26 page 69, and Table 27 page 70), there was a much reduced ^{24}Na peak and the ^{97}Zr peak was not greatly affected by the change in the neutron energy spectrum. For the samples in question, the average ^{97}Zr counts per mg of sample mass was 124 ± 1 compared to 129 ± 1 obtained earlier. This reduction is possibly a consequence of the shorter waiting periods used during the tests with Cd.

Since most of the ^{97}Zr activity arose from the resonance capture of epithermal neutrons, a useable ^{97}Zr peak could be obtained both with and without Cd foil. These values were normalized with respect to the specific activity of ^{97}Zr for each sample (Table 31), as was also the case for the analysis of residual sodium.

Table 31 The normalized values for ^{24}Na, ^{28}Al, and ^{29}Al.

Sample number	$^{24}Na/^{97}Zr$	$^{28}Al/^{97}Zr$	$^{29}Al/^{97}Zr$
1c	1.82 ± 0.10	4.93 ± 0.38	0.10 ± 0.04
Hy146	0.22 ± 0.01	7.65 ± 0.15	0.15 ± 0.01
Hy288	0.41 ± 0.02	6.43 ± 0.14	0.10 ± 0.01
Hy347	0.17 ± 0.02	8.15 ± 0.17	0.15 ± 0.01
Hy471	0.06 ± 0.02	7.80 ± 0.19	0.16 ± 0.02
Hy477	0.05 ± 0.01	7.73 ± 0.15	0.13 ± 0.02

It was worth calculating the residual sodium levels from the Cd results for comparison with the results obtained previously in the thermal plus epithermal fluxes (Table 32). This was accomplished by dividing the $^{24}Na/^{97}Zr$ ratios by a theoretical ratio calculated for a Na NASICON precursor (x = 1.5) which is assumed to have been irradiated in an epithermal flux (on the basis of a 5% epithermal flux).

$$\frac{^{24}Na}{^{97}Zr} = 49.9 \times 0.5 \times \frac{I_{23Na}}{I_{97Zr}}$$

$$= 25.0 \times 0.32/5.1$$

$$= 1.6 \qquad (16)$$

Table 32 The sodium residues calculated for sample irradiated in Cd foil

sample number	sodium residue without Cd [%]	sodium residue with Cd [%]
1c	90.7	116 ± 6
Hy146	9.59	14 ± 1
Hy288	19.8	26 ± 1
Hy347	7.51	11 ± 1
Hy471	2.24	4 ± 1
Hy477	1.30	3 ± 1

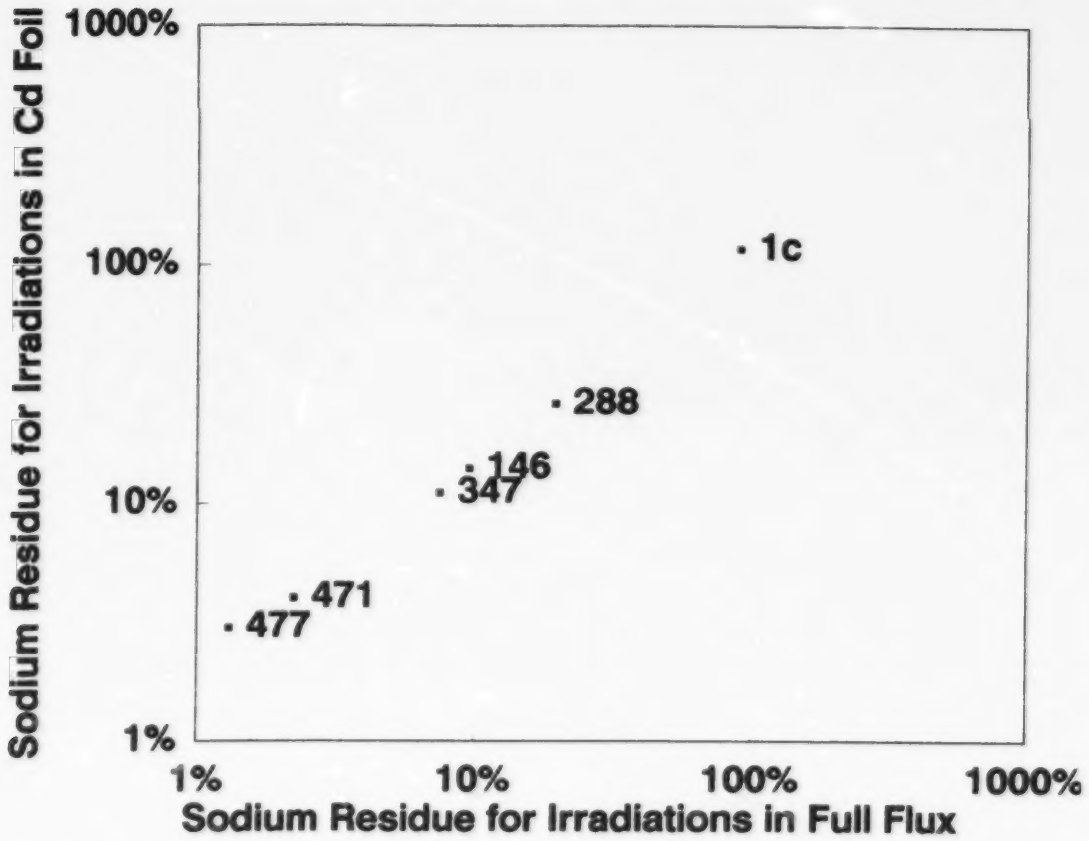


Fig. 16 The sodium residue calculated from the irradiations in Cd vs. the sodium residue calculated from the irradiations with no Cd. The ratio method was used in both cases.

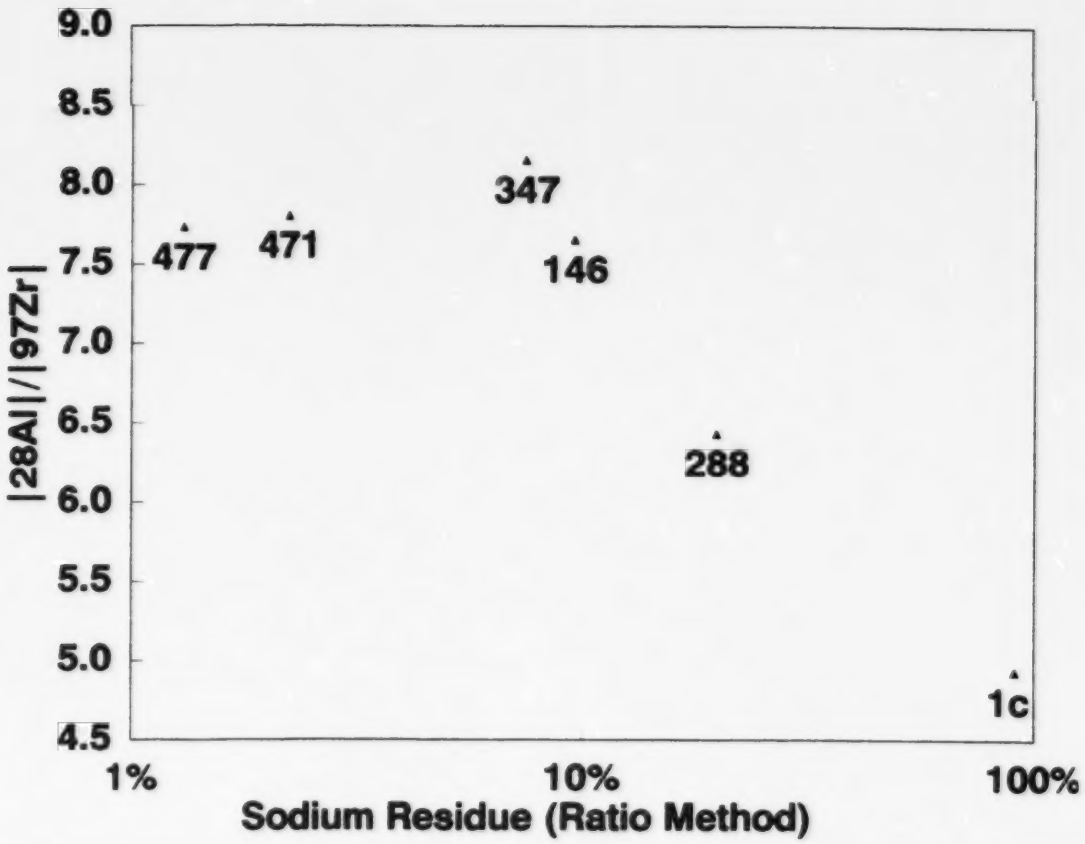


Fig. 17 The ^{28}Al peak area normalized with respect to the ^{97}Zr peak area is plotted with respect to the sodium residues calculated by the ratio method for irradiations in the full flux. The ^{28}Al arises from three sources: the silicon, the phosphorus, and the aluminum contaminant.

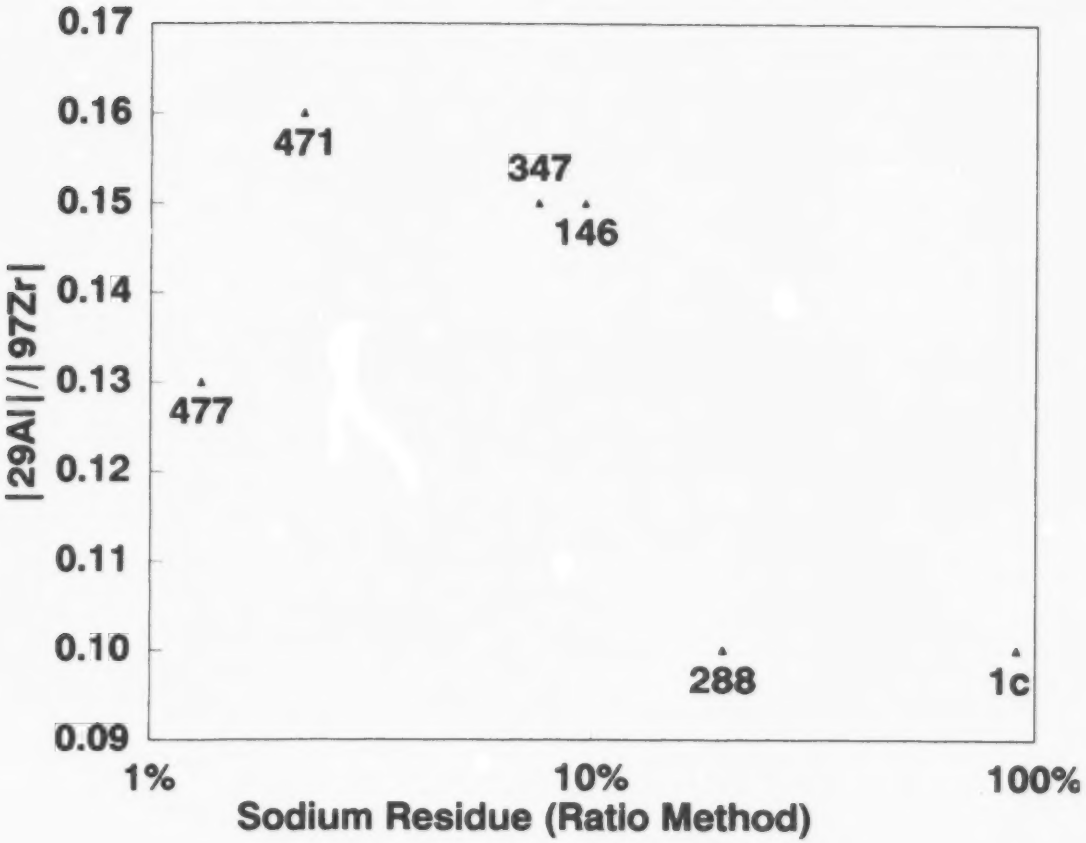


Fig. 18 The ^{29}Al peak area normalized with respect to the ^{97}Zr peak area is plotted against the sodium residues calculated by the ratio method for irradiations in the full flux. Aluminum-29 (^{29}Al) arises from the reaction of silicon with fast neutrons.

The results of the fast neutron experiments are not conclusive. One can observe an overall increase in the specific ^{28}Al activity for the pellets with respect to the powder sample since the bonding stage required the addition of phosphoric acid to the powder. The specific ^{29}Al counts are highly scattered and appear to increase with decreasing sodium residue. This quantity should stay constant or decrease a little if there is leaching of other elements from the NASICON.

7.3 XRF

XRF was used for the analysis of four Hyceram pellets. In addition to confirming the INAA results, it was possible to make a rough estimate of the amount of phosphorus added to the powder during the bonding process.

Tables 33 to 37 present the results for pellets Hy231, Hy328, Hy393, and Hy486. First, the proportions of oxides in an stoichiometric Na NASICON precursor (ϵ=100%), an optimally exchanged powder with only structural sodium (ϵ=40%), and a fully (or over) exchanged sample (ϵ=0%) are presented as examples. From the first example, the stoichiometric Na NASICON, a standard ratio of Na_2O to ZrO_2 is calculated. The standard ratio is needed for determining the fraction of residual sodium remaining in the Hyceram pellets. The results of INAA (ratio method and mass normalization method) and X-ray fluorescence are presented in Table 38 at the end of this section.

Table 33 The mass of Na_2O (measured in grams) contained in one mole of NASICON. Each of these figures is based upon the stoichiometry of: Na NASICON precursor (x = 1.5), an optimally exchanged NASICON powder (structural sodium remaining), and a fully or over exchanged NASICON powder (no sodium remaining).

	Mass of Na_2O (grams) in one mole of NASICON
Na NASICON Precursor (ϵ=100%):	77.47
Optimally exchanged Hydronium NASICON (ϵ=40%):	30.99
Fully (over) exchanged Hydronium NASICON (ϵ=0%):	0.00

Table 34 The proportions of oxides in the NASICON powders based on the stoichiometry of: Na NASICON precursor (x = 1.5), an optimally exchanged NASICON powder (structural sodium remaining), and a fully or over exchanged NASICON powder (no sodium remaining).

	Precursor no exchange	optimally exchanged	fully (over) exchanged
Na_2O	3144	1257	0
ZrO_2	10000		
P_2O_5	4320		
SiO_2	3657		
TOTAL	21121	19234	17977

Table 35 The proportions of oxides in the four samples of Hyceram. The units are in weight percent.

	Hy231	Hy328	Hy393	Hy486
Na_2O	0.42	0.56	1.01	0.00
ZrO_2	43.94	45.03	43.63	49.99
P_2O_5	28.45	30.32	29.91	30.35
SiO_2	17.49	14.81	14.00	14.45
Al_2O_3	0.59	0.46	0.66	0.29
BALANCE	9.11	8.82	10.79	4.92

Table 36 Normalized proportions of oxide in the four samples of Hyceram produced by dividing the amount of oxide by the amount of ZrO_2 and multiplying by 10000.

	Hy231	Hy328	Hy393	Hy486
Na_2O	96	124	232	0
ZrO_2	10000	10000	10000	10000
P_2O_5	6475	6733	6855	6071
SiO_2	3980	3289	3209	2891
Al_2O_3	143	102	151	58
BALANCE	2073	1959	2473	984
TOTAL	22767	22207	22920	20004

Table 37 The quantities of Na_2O, P_2O_5, and SiO_2 in the four pellets of Hyceram. The units are in percent. Values less than 100 indicate a reduction in the quantity of the oxide with respect to the stoichiometric quantity; values greater than 100 indicate that the amount of the oxide has been increased as a result of additions. Additions include deliberate combining of phosphoric acid during the binding process and uncontrolable contamination of the powder during processing.

	Hy231	Hy328	Hy393	Hy486
Na_2O	3.1	3.9	7.4	0
P_2O_5	150	156	159	141
SiO_2	109	90	88	79

Table 38 shows the sodium residue values obtained by the ratio method, the mass normalization method, and X-ray fluorescence. The three methods produced values which are of the same order for each sample. In general, the X-ray fluorescence method produces sodium residues which are lower than the values obtained by INAA; this is a consequence of sodium having a small atomic number (Z = 11). Otherwise, the X-ray fluorescence method is an effective means of measuring the amounts of P_2O_5, Al_2O_3, SiO_2, and ZrO_2 in the samples.

It may be concluded that the X-ray fluorescence results support the results of the INAA, and that a large fraction of the structural sodium was removed from the NASICON powder during the ion exchange process.

Table 38 The sodium residues for four samples of Hyceram determined by INAA (the ratio method and mass normalization method) and X-ray fluorescence.

	SODIUM RESIDUES [%]		
sample number	Neutron Activation Analysis		X-ray fluorescence
	ratio method	mass norm. method	
Hy231	6.07	5.16	3.1
Hy328	7.66	6.69	4.0
Hy393	9.14	8.44	7.4
Hy486	1.30	1.20	0.0

7.4 Discussion of Results of Testing of Pellets

The use of INAA with either the mass normalization method or the ratio method confirmed that the pellets made from Hydronium NASICON which had been exchanged once still contained a quantity of residual sodium (6% to 20%). The pellets made from Hydronium NASICON which had been exchanged four times contained less residual sodium than those in the earlier series. Neither of the two normalization methods were exact; the mass normalization method yielded values which were low since phosphoric acid had been added to the powder during the preparation of the pellets. The ratio method was more exact, although its results were slightly lower than the true values since there was extra zirconia in

the Hydronium NASICON powder. The ratio method appeared to be the best of the two methods when testing pellets; but either method could be used when testing the NASICON powders.

The use of the fast neutron flux for measuring the amounts of phosphorus and silicon in the Hyceram pellets proved to be technically difficult and too inaccurate to provide useful results. The XRF results suggested that phosphorus which was added during the bonding procedure accounted for 10% of the sample mass. In future, quantification of the manufacturing process would be a valuable approach for determining the amount of intergranular phase in the pellets.

8 Conclusions

1. INAA has been shown to be a useful technique for the study of the sodium content of NASICON powders and Hyceram pellets. The unreactive nature of zirconium during ion exchange, and its nuclear characteristics, make it useful as an alternative normalization factor; sample mass is the traditional choice, but the possible loss of material from the exchanged powders during ion exchange, variation in moisture content, and the addition of binder to make Hyceram, changes the sample's mass and makes the calculation of sodium residues difficult to standardize.

2. Sodium residues were reduced to below 1% by the use of repeated ion exchange steps. This demonstrates that the structural sodium is exchangeable and confirms the theory that sodium conduction occurs by the movement of sodium ions through the structural site. The sodium residue measurements were confirmed by the use of XRF on the powders, and ICP on the waste acid solutions.

3. The XRD patterns indicated that the basic crystal structure of NASICON deviates from the rhombohedral structure of the precursor in the intermediate stages of ion exchange, but returns to a rhombohedral structure once the final product (hydronium NASICON) is produced. The C axis increased in length by 5% while the A axis decreased in length by 2%, upon completion of the ion exchange process.

4. The analysis of silicon and phosphorus concentrations by INNA was not successful even when using the epi-thermal flux. XRF proved to be the best method of measuring these elements. There was a 40 to 60% greater quantity of P_2O_5 in the Hyceram pellets than in the stoichiometric powder. This was expected since phosphoric acid was used in the bonding process. The silicon levels in the Hyceram were slightly lower than the level in the stoichiometric powder. This is possibly a result of the acid treatment and may account for the reduction in the powders' sample masses inferred from the INAA results.

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